

JTW

SOLUTIONS MANUAL to accompany

Instrumental Analysis

SECOND EDITION

Gary D. Christian

James E. O'Reilly

Solutions Manual
to Accompany
Instrumental Analysis

**Solutions Manual
to Accompany
Instrumental Analysis**

| Second Edition

Editors

GARY D. CHRISTIAN
University of Washington

JAMES E. O'REILLY
University of Kentucky

Allyn and Bacon, Inc.
Boston London Sydney Toronto



Copyright © 1986 by Allyn and Bacon, Inc., 7 Wells Avenue,
Newton, Massachusetts 02159. All rights reserved. No
part of the material protected by this copyright notice may
be reproduced or utilized in any form or by any means,
electronic or mechanical, including photocopying, recording,
or by any information storage and retrieval system, without
written permission from the copyright owner.

ISBN 0-205-08641-1

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1 91 90 89 88 87 86

CHAPTER 1

1. From Eqn. 1.6,

$$\begin{aligned}
 c &= \frac{i \pi^{\frac{1}{2}} t^{\frac{1}{2}}}{nFAD^{\frac{1}{2}}} \\
 &= \frac{(10^{-6} \text{ coul/sec})(\text{sec})^{\frac{1}{2}}}{(\text{Faradays/mole})(\text{coul/Faraday})(\text{cm}^2)(\text{cm}^2/\text{sec})^{\frac{1}{2}}} \\
 &= \frac{10^{-6} \text{ mole}}{\text{cm}^3} = \frac{10^{-3} \text{ mole}}{1} = \underline{mM}
 \end{aligned}$$

2. $0^\circ\text{C} = 273.16\text{K}$; $100^\circ\text{C} = 373.16\text{K}$

$$\text{Body Temperature (98.6}^\circ\text{F}): \frac{5(98.6 - 32.0)}{9} = 37.0^\circ\text{C} = 310.16\text{K}$$

$$\begin{aligned}
 \text{At } 0^\circ\text{C}, \frac{2.303 \text{ RT}}{nF} &= \frac{2.303 (8.314 \text{ J/mole - K}) (273.16\text{K})}{96487 \text{ coulombs/mole}} \\
 &= 0.05420/n \text{ J/coulomb} = 0.05420/n \text{ V}
 \end{aligned}$$

In a similar manner, $0.06154/n$ and $0.07404/n$ V at body temperature and at 100°C , respectively.

3. From Eqn. 1.6,

$$\text{Charge} = q = \text{coulombs} = \int_0^t i dt = \int_0^t \frac{nFAD^{\frac{1}{2}} c}{\pi^{\frac{1}{2}} t^{\frac{1}{2}}} dt$$

$$= \frac{nFAD^{\frac{1}{2}}c}{\pi^{\frac{1}{2}}} \int_0^t t^{-\frac{1}{2}} dt$$

$$= \frac{2nFAD^{\frac{1}{2}}c t^{\frac{1}{2}}}{\pi^{\frac{1}{2}}}$$

4. From Eqn. 1.1, $q = CV$

Now, current i is coulombs/sec or dq/dt .

$$\text{Therefore, } i = \frac{dq}{dt} = \frac{d}{dt} (CV) = C \frac{dV}{dt} = Cv$$

assuming the capacitance of the electrode does not change with time.

5. From Eqn. 1.1,

$$q = CV = (20 \times 10^{-6} \text{ F/cm}^2) (0.50 \text{ cm}^2) (-1.00 \text{ V}) = 1.0 \times 10^{-5} \text{ coulombs}$$

The number of metal atoms on the surface of an electrode of 0.50 cm^2 area would be

$$n = \frac{0.50 \text{ cm}^2}{(15 \text{ \AA}^2/\text{atom}) (10^{-8} \text{ cm}/\text{\AA})^2} = 3.33 \times 10^{14} \text{ atoms}$$

$$e/\text{atom} = \frac{1.0 \times 10^{-5} \text{ coulombs} (6.022 \times 10^{23} \text{ e/Faraday})}{(96487 \text{ coul/Faraday}) (3.33 \times 10^{14} \text{ atoms})} = 0.187 = 0.2$$

or approximately 1 excess surface electron per 5 metal atoms.

6. From Eqn. 1.3,

$$(\text{Red})/(\text{Ox}) = 10^{(E^\circ - E)/0.05916 \text{ V}}$$

If $E = E^\circ$, then $(\text{Red})/(\text{Ox}) = 1$.

It would make no difference what the ratio of $(\text{Red})/(\text{Ox})$ forms is in the bulk of the solution. If the couple were behaving reversibly, enough current would be passed at the electrode surface to make the surface ratio equal to 1.

If E is 10 mV negative of E° , $(E^{\circ}-E) = +10$ mV, then

$$(Red)/(Ox) = 10^{(+10 \text{ mV}/59.16 \text{ mV})} = 1.48$$

In a similar manner, the ratio is 49, 2400, 2.8×10^8 , and 8.0×10^{16} for 100, 200, 500, and 1000 mV potentials, respectively.

7. For $R = 1\Omega$ and $C = 5\mu\text{F}$,

$$RC = 1\Omega (5 \times 10^{-6} \text{ F}) = 5 \times 10^{-6} \text{ sec} \text{ (see Appendix A for equivalency of units)}$$

Similarly, $RC = 50$ and $500 \mu\text{sec}$ for 10 and 100Ω .

For $R = 1\Omega$ and $\Delta E_{\text{applied}} = 100$ mV

$i_0 = \Delta E_{\text{applied}}/R = 0.100 \text{ V}/1\Omega = 0.100\text{A}$, a very large current for most electrochemical measurements.

Similarly, $i_0 = 10^{-2}$ and 10^{-3} A for $R = 10$ and 100Ω .

From $i = i_0 e^{-t/RC}$, $t = RC \ln(i_0/i)$

For 1Ω , $t = (5\mu\text{sec}) \ln(10^{-1}\text{A}/10^{-9}\text{A}) = 92 \mu\text{sec}$

Similarly, $t = 806 \mu\text{sec}$ and 6.9 msec for 10 and 100Ω .

CHAPTER 2

$$1. \quad E = E_{\text{constant}} + \frac{RT}{nF} \ln a_i$$

$$\frac{dE}{da} = \frac{RT}{nF}$$

$$\frac{da}{a} = \frac{nF}{RT} \frac{dE}{da}$$

$$\frac{\Delta a}{a} = \text{relative concentration error} = \frac{nF(\Delta E)}{RT}$$

$$\text{at } 25^\circ\text{C with } \Delta E = 0.001 \text{ V, } \frac{\Delta a}{a} = 0.039n \text{ or } 3.9n \%$$

$$2. \quad \text{a) In } 0.01 \text{ M } \text{CaCl}_2, [\text{Ca}^{2+}] = 0.01 \text{ and } [\text{Cl}^-] = 0.01$$

For Ca^{2+} , $z = 2$; for Cl^- , $z = 1$

$$\text{Since } I = \frac{1}{2} \sum c_i z_i^2,$$

$$I = \frac{1}{2}[(0.01)(2)^2 + (0.02)(1)^2] = 0.03 \text{ M}$$

b) Likewise, in 0.05 M KCl,

$$I = \frac{1}{2}[(0.05)(1)^2 + (0.05)(1)^2] = 0.05 \text{ M}$$

c) In 0.1 M Na_2SO_4 ,

$$I = \frac{1}{2}[(0.2)(1)^2 + (0.1)(2)^2] = 0.3 \text{ M}$$

d) In 0.001 M AlCl_3 ,

$$I = \frac{1}{2}[(0.001)(3)^2 + (0.003)(1)^2] = 0.006 \text{ M}$$

3. a) In 0.002 M MgCl_2 ,

first calculate I:

$$I = \frac{1}{2}[(0.002)(2)^2 + (0.004)] = 0.006 \text{ M}$$

then calculate f:

$$-\log f_{\text{Mg}^{2+}} = 0.5 z^2 \frac{I}{\text{Mg}^{2+}} = (0.5)(2)^2 (0.006)^{\frac{1}{2}} = 0.155$$

$$f_{\text{Mg}^{2+}} = 0.70$$

$$-\log f_{\text{Cl}^-} = 0.5(1)^2(0.006)^{\frac{1}{2}} = 0.039; \text{ so } f_{\text{Cl}^-} = 0.91$$

b) In a 0.002 M MgCl_2 + 0.01 M KCl mixture:

$$[\text{Mg}^{2+}] = 0.002, [\text{Cl}^-] = 0.014, [\text{K}^+] = 0.01$$

$$\text{So, } I = 0.016$$

$$-\log f_{\text{Mg}^{2+}} = (0.5)(2)^2(0.016)^{\frac{1}{2}}, f_{\text{Mg}^{2+}} = 0.56$$

$$-\log f_{\text{K}^+} = (0.5)(1)^2(0.016)^{\frac{1}{2}}, f_{\text{K}^+} = 0.86$$

$$-\log f_{\text{Cl}^-} = (0.5)(1)^2(0.016)^{\frac{1}{2}}, f_{\text{Cl}^-} = 0.86$$

c) Here, $[\text{Mg}^{2+}] = 0.002, [\text{K}^+] = 0.1, [\text{Cl}^-] = 0.104$

$$\text{So, } I = 0.106$$

$$-\log f_{\text{Mg}^{2+}} = (0.5)(2)^2(0.106)^{\frac{1}{2}}, f = 0.22$$

$$-\log f_{\text{K}^+} = (0.5)(1)^2(0.106)^{\frac{1}{2}}, f = 0.69$$

$$-\log f_{\text{Cl}^-} = (0.5)(1)^2(0.106)^{\frac{1}{2}}, f = 0.69$$

4. a) $\frac{(a_{\text{H}^+})(a_{\text{A}^-})}{a_{\text{HA}}} = 1.75 \times 10^{-5}$ where A^- is CH_3COO^-

Assume $a_{\text{HA}} = [\text{HA}] = 0.03$, since it is neutral.

$$a_{\text{A}^-} = f_{\text{A}^-} [\text{A}^-]$$

Now calculate f_{A^-} from I and the Debye-Hückel expression

$$I = \frac{1}{2}[(\text{K}^+)(1)^2 + (\text{Cl}^-)(1)^2 + (\text{A}^-)(1)^2 + (\text{Na}^+)(1)^2]$$

$$= \frac{1}{2}[0.1 + 0.1 + 0.02 + 0.02] = 0.12$$

$$-\log f_{A^-} = (0.5) (1)^2 (0.12)^{\frac{1}{2}} = 0.173$$

$$f_{A^-} = 0.67$$

$$a_{A^-} = 0.67 (0.02) = 0.0134$$

$$\frac{(a_{H^+})(0.0134)}{0.03} = 1.75 \times 10^{-5}$$

$$a_{H^+} = 3.92 \times 10^{-5}$$

$$pH = -\log a_{H^+} = 4.41$$

$$b) \frac{(a_{H^+})(a_{CH_3NH_2})}{a_{CH_3NH_3^+}} = 2.0 \times 10^{-11}$$

$$f_{CH_3NH_3^+} = 0.67 \text{ as } I \text{ and } z \text{ are the same as in part (a)}$$

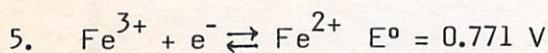
$$a_{CH_3NH^+} = (0.67)(0.03) = 0.02$$

The acid is $CH_3NH_3^+$ and the conjugate base is CH_3NH_2

$$f_{CH_3NH_3} = 1.0 \text{ (neutral species)}$$

$$\frac{(a_{H^+})(0.02)}{(0.02)} = 2.0 \times 10^{-11}$$

$$a_{H^+} = 2.0 \times 10^{-11} \quad pH = 10.7$$



$$E = 0.771 - \frac{0.059}{1} \log \frac{0.1}{0.2} = 0.789 \text{ V}$$

Since the SCE is 0.245 V positive of the SHE, this half-cell is only $0.789 - 0.245 = 0.544 \text{ V}$ positive of the SCE.

6. $\text{Ag}/\text{AgNO}_3, 1 \text{ M}/\text{KI}, 1 \text{ M}, \text{AgI}(\text{sat'd})/\text{Ag}$

Both half-cell reactions involve $\text{Ag}^+ + \text{e} \rightleftharpoons \text{Ag}$ $E^\circ = 0.799 \text{ V}$

$$E_{\text{Right}} = 0.799 - \frac{0.059}{1} \log \frac{1}{[\text{Ag}^+]_{\text{Right}}}$$

$[\text{Ag}^+]_{\text{Right}}$ can be expressed in terms of $[\text{I}^-]$ and K_{sp} :

$$[\text{Ag}^+]_{\text{Right}} = \frac{K_{\text{sp}}}{[\text{I}^-]}$$

$$E_{\text{Right}} = 0.799 - \frac{0.059}{1} \log \frac{[\text{I}^-]}{K_{\text{sp}}} = 0.799 + 0.059 \log K_{\text{sp}} - 0.059 \log [\text{I}^-]$$

$$= 0.799 + 0.059 \log (8.3 \times 10^{-17}) - 0.059 \log (1.0) = -0.150 \text{ V}$$

$$E_{\text{Left}} = 0.799 + \frac{0.059}{1} \log \frac{1}{[\text{Ag}^+]} = 0.799 - 0.059 \log 1 = 0.799 \text{ V}$$

$$E_{\text{cell}} = E_R - E_L = -0.150 - 0.799 = -0.949 \text{ V}$$

7. a) $E_{\text{cell}} = E_R - E_L$; $E_R = E_{\text{Ag}} = E_{\text{cell}} + E_L$; also $E_L = E_{\text{SCE}} = 0.245 \text{ V}$

$$E_{\text{Ag}} = 0.323 \text{ V} + 0.245 \text{ V} = 0.568 \text{ V}$$

$$\text{Now, } E_{\text{Ag}} = 0.799 - 0.059 \log \frac{1}{[\text{Ag}^+]}$$

$$\text{or, } 0.568 = 0.799 - 0.059 \log \frac{1}{[\text{Ag}^+]}$$

$$\text{Ag}^+ = 1.2 \times 10^{-4} \text{ M}$$

b) $[\text{Ag}^+] = 1.2 \times 10^{-4}$, $[\text{Na}^+] = 0.01$, $[\text{NO}_3^-] = 1.2 \times 10^{-4} + 0.01$

$$I = 0.0101 \approx 0.01 \text{ M}$$

$$-\log f_{Ag^+} = 0.5 (1)^2 (0.01)^{\frac{1}{2}}$$

$$f_{Ag^+} = 0.89$$

$$E_{Ag} = 0.799 - 0.059 \log \frac{1}{(1.2 \times 10^{-4})(0.89)}$$

$$E_{Ag} = 0.565 \text{ V}$$

$$E_{cell} = E_R - E_L = 0.565 \text{ V} - 0.245 \text{ V} = 0.320 \text{ V}$$

c) $Q = it = (10^{-4} \text{ amps}) (20 \text{ sec}) = 2 \times 10^{-3} \text{ coulombs}$

There are 96,500 coulombs per equivalent, so the electrolysis causes a change of $(2 \times 10^{-3})/(9.65 \times 10^4) = 2 \times 10^{-8}$ equivalents

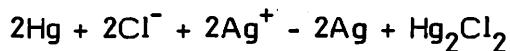
Since $n = 1$, the mole-change is also 2×10^{-8} . A change of 2×10^{-8} moles in 5 ml corresponds to a change of $4 \times 10^{-6} \text{ M}$.

d) At equilibrium $E_{cell} = 0$, so $E_R = E_L = 0.245 \text{ V}$

$$0.245 = 0.799 - 0.059 \log \frac{1}{[Ag^+]}$$

$$Ag^+ = 4 \times 10^{-10} \text{ M}$$

The more positive half-cell undergoes reduction:



8. First, assume all activity coefficients are 1.0. Second, recognize that we must convert mg/l to molarities.

$$400 \text{ mg Ca/l} = 0.010 \text{ moles Ca/l}$$

$$1300 \text{ mg Mg/l} = 0.053 \text{ moles Mg/l}$$

$$(k_{Ca/Mg}) [Mg^{2+}] = (0.014)(0.053) = 7.5 \times 10^{-4}$$

The true $[Ca^{2+}] = 1.0 \times 10^{-2}$; the Mg^{2+} "acts like" an additional 7.5×10^{-4} moles Ca/l.

$$\text{The resulting \% error is } \frac{(7.5 \times 10^{-4})(100)}{1.0 \times 10^{-2}} = 7.5\%$$

9. Assume all activity coefficients are 1.0.

From $E = \text{const} + \frac{0.059}{n} \log (a_i + k_{ij} a_j^{n/z})$, we are to determine the concentration of interfering ion j that yields $k_{ij} a_j^{n/z}$ equal to 1% (or 10%) of the concentration of test ion i . $i = \text{Ca}^{2+} = 10^{-4} \text{ M}$; 1% of $10^{-4} \text{ M} = 10^{-6} \text{ M}$

When $j = \text{Zn}^{2+}$, $n = z = 2$ and $k = 3.2$, so $3.2 [\text{Zn}^{2+}] = 10^{-6}$ or

$[\text{Zn}^{2+}] = 3.1 \times 10^{-7}$, which responds the same as $10^{-6} \text{ M Ca}^{2+}$;

when $j = \text{Fe}^{2+}$, $(0.80) [\text{Fe}^{2+}] = 10^{-6} \text{ M}$ or $[\text{Fe}^{2+}] = 1.25 \times 10^{-6}$;

when $j = \text{Pb}^{2+}$, $(0.63) [\text{Pb}^{2+}] = 10^{-6} \text{ M}$ or $[\text{Pb}^{2+}] = 1.6 \times 10^{-6}$;

when $j = \text{Mg}^{2+}$, $(0.014) [\text{Mg}^{2+}] = 10^{-6} \text{ M}$ or $[\text{Mg}^{2+}] = 7.1 \times 10^{-5}$;

when $j = \text{Na}^+$, $n = 2$ and $z = 1$, so $(0.003) [\text{Na}^+]^2 = 10^{-6} \text{ M}$ or $[\text{Na}^+] = 1.8 \times 10^{-2}$.

For a 10% interference on $10^{-4} \text{ M Ca}^{2+}$, $K_{ij} [j]^{n/z} = 0.1 (10^{-4}) \text{ M}$

All answers will be 10 times larger except for Na^+ where

$(0.003) [\text{Na}^+]^2 = 10^{-5}$ and $[\text{Na}^+] = 5.8 \times 10^{-2}$, or 3.2 times larger.

10. First calculate Δc by $\Delta c = \frac{(0.100 \text{ ml})(0.500 \text{ mg/ml})}{25.00 \text{ ml} + 0.100 \text{ ml}}$ or $\Delta c = 1.99 \times 10^{-3} \text{ mg/ml}$

$$E_1 = -155.3 \text{ mV} = -0.1553 \text{ V} \text{ and } E_2 = -176.2 \text{ mV} = -0.1762 \text{ V}$$

$$\text{Since } n = -1 \text{ for } F^-, E_2 - E_1 = -0.0592 \log \frac{(c + \Delta c)}{c}, \frac{0.0209}{0.0592} = \log \frac{c + \Delta c}{c}$$

$$\text{Then } 2.25 = \frac{c + 1.99 \times 10^{-3}}{c} \text{ with } c \text{ in mg/ml}$$

$$c = 1.59 \times 10^{-3} \text{ mg/ml.}$$

The measured aliquot, 25.00 ml, contains $(1.59 \times 10^{-3})(25.00)$ mg F^- , but the total sample contains 4 times this value or 0.159 mg F^- .

$$\%F = \frac{0.159 \text{ mg}}{200 \text{ mg}} \times 100 = 0.0795\% F$$

11. addition	Δc , moles/l	$(E_2 - E_1)/S$	$10(E_2 - E_1)/S$
100 μ l	3.91×10^{-6}	+0.247	1.76
(100+100) μ l	7.81×10^{-6}	+0.403	2.53
(200+200) μ l	1.56×10^{-5}	+0.605	4.03
(400+200) μ l	2.32×10^{-5}	+0.744	5.55

(note: $S = -59.2 \text{ mV}$ since $n = -1$)

$$\Delta c = \frac{(\text{ml added}) ([I^-])}{(\text{total volume, ml})}$$

plot $10 \Delta E/S$ vs Δc ; intercept is $-0.45 \times 10^{-5} \text{ M } I^-$. The intercept represents the amount of I^- that would have to be "removed" from solution to make $10 \Delta E/S = 0$. In other words, the original solution contained $4.5 \times 10^{-6} \text{ M } I^-$.

$$4.5 \times 10^{-6} \frac{\text{moles}}{\text{l}} \times 127 \frac{\text{g } I}{\text{mole}} \times \frac{(1 \text{ l})}{10^3 \text{ ml}} \times \frac{(10^6 \text{ } \mu\text{g})}{\text{g}} = 0.57 \text{ } \mu\text{g/ml}$$

12. a) The ISE only responds to the "free" ion, so the expected result is

$$(0.75)(4 \times 10^{-5}) \underline{M} = 3 \times 10^{-5} \underline{M} \text{Ca}^{2+}$$

b) If the complexing agent is in large excess, 25% of the added Ca will be tied up.

The fraction that changes the electrode potential will be the same as the "free" fraction of the unknown. As a result, the answer will be the total Ca in solution, $4 \times 10^{-5} \underline{M}$.

13. The slope, $\frac{0.059}{n} \text{ V}$, is lower as n increases; sensitivity is related to the slope of

calibration curves. More interference occurs since lower charged ions tend to be more mobile in crystals, so there is more likely to be a monovalent ion interference with a sensor for a divalent ion than vice versa. Further, the activity of the interferent is raised to the n/z power in the response equation.

$$14. E_1 = A + S \ln a_i$$

$$E_2 = A + S \ln (a_i + k_{ij} a_j)$$

$$E_2 - E_1 = S \ln \frac{(a_i + k_{ij} a_j)}{a_i}$$

Divide by S , substitute $S = \frac{2.3 RT}{nF}$ (or determine S empirically

from measurements of two or more concentrations of a_i), and change \ln to \log :

$$\frac{n(E_2 - E_1)F}{2.3RT} = \log \frac{(a_i + k_{ij} a_j)}{a_i}$$

$$10^{[n(E_2 - E_1)F]/2.3RT} = \frac{a_i + k_{ij} a_j}{a_i} = 1 + k_{ij} \frac{a_j}{a_i}$$

$$15. 10^{\Delta E/S} = k_{ij} \frac{a_j}{a_i} + 1$$

Assume $f_{\text{Br}^-} = f_{\text{I}^-}$ and constant liquid junction potentials

<u>solution</u>	<u>[Br⁻]/[I⁻]</u>	<u>10^{ΔE/S}</u>
1	100	1.05
2	300	1.15
3	700	1.33
4	1100	1.51

From a plot (calculating the slope) or by solving the equation for each entry,
 $k_{ij} = 5 \times 10^{-4}$. Note: you must correct for dilution of the 1×10^{-4} M I⁻ after each
 standard addition. You must also recognize that S is negative.

16.	<u>ml</u>	<u>mV</u>	<u>Δ(mV)</u>	<u>Δ^2(mV)</u>
	47.60	372		
			12	
	47.70	384		5
			17	
	47.80	401		94
			111	
	47.90	512		109
			220	
	48.00	732		-204
			16	
	48.10	748		-8
			8	
	48.20	756		

The division by Δml is unnecessary, since Δml is constant. The first derivative endpoint is at the peak of $\Delta(mV)/\Delta(ml)$ vs ml (ave) (or ΔmV vs. ml (ave) in our case). The second derivative endpoint is where the plot of $\Delta^2 mV$ vs ml goes through zero (i.e., between 47.90 and 48.00 ml). The latter is more precise and easier to identify, as a straight line is used to connect +109 and -204. The correct value is 47.93 ml.

17. $E = \text{const} + \frac{59}{n} \log [\text{Ca}^{2+}]$

$63.3 = \text{const} + 29.5 \log (0.01)$ since $n = 2$

$\text{const} = 122.3 \text{ mV}$

With $10^{-2} \text{ M Zn}^{2+}$ ($z = 2$), $113.6 \text{ mV} = 122.3 \text{ mV} + 29.5 \log k_{ij} [\text{Zn}^{2+}]$

$$k_{ij} = 50.7;$$

$$\text{for } \text{Pb}^{2+}, 101.8 = 122.3 + 29.5 \log k (10^{-2}), k = 20.2;$$

$$\text{for } \text{Mg}^{2+}, 4.2 = 122.3 + 29.5 \log k (10^{-2}), k = 0.01.$$

$$\text{For } \text{H}^+, \text{Na}^+ \text{ and } \text{K}^+, z = 1 \text{ but } n = 2;$$

$$\text{for } \text{H}^+, 92.9 = 122.3 + 29.5 \log [k(0.01)^2], k = 1000;$$

$$\text{for } \text{Na}^+, -70.4 = 122.3 + 29.5 \log [k(0.01)^2], k = 2.9 \times 10^{-3};$$

$$\text{for } \text{K}^+, -84.6 = 122.3 + 29.5 \log [k(0.01)^2], k = 9.7 \times 10^{-4}.$$

CHAPTER 3

$$1. \quad i_d = 708 n D^{\frac{1}{2}} m^{2/3} t^{1/6} c = (708) (2) (6 \times 10^{-6})^{\frac{1}{2}} (2)^{2/3} (5)^{1/6} (1) \mu A$$

$$i_d = 7.2 \mu A$$

$$2. \quad i_d \propto m^{2/3} t^{1/6}$$

$$m \propto h$$

$$t \propto 1/h$$

$$\text{so, } i_d \propto h^{2/3} / h^{1/6}$$

$$i_d \propto h^{\frac{1}{2}}$$

3. <u>E</u>	<u>i</u>	$\log \frac{i}{i_d - i}$
-0.475 V	0.62 μA	-0.849
-0.490 V	1.57 μA	-0.339
-0.510 V	3.43 μA	0.339
-0.525 V	4.38 μA	0.849

Plot E vs. $\log \frac{i}{i_d - i}$; a straight line is obtained. From the slope, -0.0294 V, and

comparison to the theoretical slope for a reversible process, $-0.059/n$ V, an n-value of 2.0 is obtained. The integral (and reasonable) n-value in conjunction with the straight line verifies the reversibility. The plot goes through zero (log 1) at $E = E_{\frac{1}{2}} = -0.500$ V.

4. a) Calibration curve: the large number of samples and the constant matrix (the white wine) makes it more efficient to use this method. If the variation of the wine

from lot-to-lot caused a change in slope of the calibration curves, then the pilot-species method would be preferable.

b) Standard addition: the calibration curve slope would have to be checked each time; therefore, the standard addition method would be more efficient. An exception to this answer would be if the standard solution were difficult to prepare and store; then the pilot-ion (internal standard) - calibration curve approach would be easier.

c) Standard addition: it would be too difficult to match the matrix.

d) Calibration curve: a constant matrix that is easily duplicated and the large number of samples to be run makes this approach by far the better choice.

5. HCl; it is readily purified by distillation. An alternative is to use a salt solution that has been purified by ion-exchange, solvent extraction or controlled potential electrolysis at a large mercury pool electrode.

6. a) $I_d = \frac{i_d}{cm^{2/3} t^{1/6}}$

$$= \frac{3.96}{(0.500)(2.50)^{2/3} (3.02)^{1/6}}$$
$$I_d = 3.58$$

b) $3.59 = 607 nD^{\frac{1}{2}}$

$$D = [3.59/(2)(607)]^2$$

$$D = 8.74 \times 10^{-6} \text{ cm}^2/\text{sec}$$

7. $(2.5 \text{ mg/sec}) (3.0 \text{ sec}) = 7.5 \text{ mg}$

The density of Hg is 13.6 gm/cm^3

$$\frac{7.5 \times 10^{-3} \text{ gm}}{13.6 \text{ gm/cm}^3} = 5.5 \times 10^{-4} \text{ cm}^3$$

$$V = 4\pi r^3/3 \text{ so } r = 0.051 \text{ cm}$$

$$A = 4\pi r^2 = 0.032 \text{ cm}^2$$

or from Eqn. 3.2:

$$A = 0.852 (mt)^{2/3} \text{ in mm}^2 = 3.26 \text{ mm}^2$$

8. $i_d = 708 nD^{1/2} m^{2/3} t^{1/6} C$

$$C = 2.11/(708) (2) (2.12 \times 10^{-5})^{1/2} (2.00)^{2/3} (5.00)^{1/6} = 0.156 \text{ mM}$$

$$(0.156 \times 10^{-3} \text{ moles/l}) (32.0 \text{ gm/mole}) = 4.99 \times 10^{-3} \text{ gm/l}$$

Therefore, the O_2 level is 4.99 mg/l or 4.99 ppm in a solvent of density 1000 gm/l.

9. $i_d = 708 nD^{1/2} m^{2/3} t^{1/6} C$

$$n = \frac{6.8}{(708) (2.2 \times 10^{-3}) (1.6) (1.3) (1.0)}$$

$$n = 2.1 \approx 2$$

10. $(E_{1/2})_{\text{cplx}} = (E_{1/2})_{\text{uncplx}} - \frac{0.059}{n} \log K_f - \frac{0.059P}{n} \log [L]$

$$-0.930 = -0.740 - \frac{0.059}{2} \log K_f - \frac{0.059(1)}{2} \log (0.20)$$

$$-0.190 = \frac{-0.059}{2} \log K_f + 0.021$$

$$K_f = 1.3 \times 10^7$$

11. a) They may decrease the effective diffusion coefficient in the vicinity of the

electrode and therefore lower the electrolysis current. In addition, they affect the double layer capacitance and hence increase the uncertainty of the residual current.

- b) No, both the electrolysis (diffusion) and the residual (capacitive) currents are increased in direct proportion to area so the ratio is unchanged. Only if the currents are so low that electronic noise in the measuring circuits limits detection will an increase in area be helpful (this is not typical).
- c) Yes, the stripping current is proportional to preelectrolysis time, at least until such point as a significant fraction of the analyte has been removed from solution and plated into (onto) the electrode. The residual current is generally unchanged. An exception would be if an interfering substance were also being accumulated (either by electrolysis or by adsorption).
- d) As long as a plateau can be developed, irreversibility will not affect DC polarography or pulse polarography wave heights, since the limiting currents are still diffusion controlled. The waves will be drawn out, so there is a greater chance of interference, and the detectability may be lessened since sharper waves are easier to detect. With differential pulse polarography the peak current (which represents the rate of change of current) will be lower because of the more gradual increase in current with the negative-going potential scan prior to the onset of pure diffusion control.
- e) Not always: if the residual current magnitude or uncertainty were also increased, the increase in electrolysis current would be offset.

12. $q = it = (4.0 \times 10^{-6} \text{ amps}) (30 \text{ min}) (60 \text{ sec/min}) = 7.2 \times 10^{-3} \text{ coul}$

There are ca. 96,500 coulombs per equivalent (the value of the Faraday), so

$$\text{equivalents} = q/F = 7.5 \times 10^{-8}$$

$$n = 2, \text{ so the moles electrolyzed} = 3.7 \times 10^{-8} = 3.7 \times 10^{-5} \text{ mmols}$$

$$\text{The mmols in the original sample} = (50 \text{ ml}) (5.0 \times 10^{-4} \text{ M}) = 2.5 \times 10^{-2}$$

$$\text{The fraction electrolyzed} = f$$

$$f = (3.7 \times 10^{-5})/(2.5 \times 10^{-2}) = 1.5 \times 10^{-3} \text{ or } 0.15\%$$

13. a) Approximately a linear i -decrease to the endpoint at ($i = 0$), and only a very slowly rising current beyond the endpoint. The current change after the endpoint is negligible; the plot is approximately L-shaped.

b) Approximately a V-shape with $i = 0$ at the endpoint.

c) With 100 mV applied: before e.p. the reduction of Ag^+ and oxidation of Ag to Ag^+ are the reactions. After the e.p., the currents will be too low to assign a reaction with any certainty.

With 600 mV applied: the reduction of Ag^+ and the oxidation of Ag to Ag^+ are the cathodic and anodic reactions, respectively, before the endpoint.

After the endpoint, the anodic reaction is the oxidation of Ag to AgCl (curve b, between +0.4 and +0.8 V) and the cathodic reaction is the discharge of the supporting electrolyte negative of 0 V (probably the reduction of H^+).

14. For a sphere, $V = 4\pi r^3/3$

$$r = (3V/4\pi)^{1/3}$$

$$\text{But } A = 4\pi r^2, \text{ therefore } A = 4\pi(3V/4\pi)^{2/3}$$

$$\text{The volume of a mercury drop} = \text{mass} / \text{density} = \text{g}/(\text{g/cm}^3)$$

$$V = \frac{(m \text{ mg/sec})(t \text{ sec})}{(d_{\text{Hg}} \text{ g/cm}^3)(1000 \text{ mg/g})} = \frac{mt}{13,534} \text{ cm}^3 = \frac{mt}{13.534} \text{ mm}^3$$

$$\text{Then, } A = 4\pi \left[\frac{3 \text{ mt}}{13.534 (4\pi)} \right]^{2/3} \text{ mm}^2 = 0.852 (\text{mt})^{2/3} \text{ mm}^2$$

15. From Problem 8, concentration of $O_2 = 0.156 \text{ mM}$

To find the equivalent area of an electrode the same size as the mercury drops used in Problem 8, use Eqn. 3.2

$$A = 0.852 (\text{mt})^{2/3} = 0.852 [(2.00)(5.00)]^{2/3}$$

$$= 3.96 \text{ mm}^2 = 3.96 \times 10^{-2} \text{ cm}^2$$

Using Eqn. 3.28, for $v = 0.10 \text{ V/sec}$ scan rate

$$i_p = k n^{3/2} A D^{1/2} c v^{1/2}$$

$$= (2.69 \times 10^5) (2)^{3/2} (3.96 \times 10^{-2}) (2.12 \times 10^{-5})^{1/2} (0.156) (0.100)^{1/2} = 6.84 \mu\text{A}$$

For $v = 1.00 \text{ V/sec}$

$$i_p = 6.84 \mu\text{A} \left(\frac{1.0 \text{ V/sec}}{0.10 \text{ V/sec}} \right)^{1/2} = 21.6 \mu\text{A}$$

The currents are 3.2 and 10.2 times the maximum limiting current at the DME.

16. a) $i_c = Cv = (20 \times 10^{-6} \text{ F/cm}^2) (3.96 \times 10^{-2} \text{ cm}^2) (0.100 \text{ V/sec})$

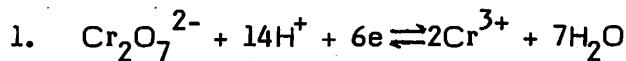
$$= 7.9 \times 10^{-8} \text{ coul/sec} = 7.9 \times 10^{-8} \text{ A} = 0.079 \mu\text{A}$$

For $v = 1.0 \text{ V/sec}$, $i_c = 0.79 \mu\text{A}$

b) At $v = 0.10 \text{ V/sec}$, $i_p/i_c = 6.84 \mu\text{A}/0.079 \mu\text{A} = 86$

For $v = 1.0 \text{ V/sec}$, $i_p/i_c = 27$

CHAPTER 4



A.W. Cr = 52.01 g/mol

$$\text{E.W. Cr} = \frac{52.01}{3} \text{ g/eq}$$

$$1\text{-} \mu\text{ coul} \times \left(\frac{1}{96,485} \text{ } \mu\text{eq}/\mu\text{-coul} \right) \left(\frac{52.01}{3} \text{ } \mu\text{g}/\mu\text{eq} \right)$$

$$= 1.797 \times 10^{-4} \text{ } \mu\text{g Cr}$$

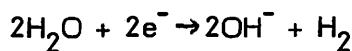
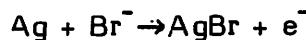
2. Net eq Br_2 needed to react olefin =

$$(50.0 \text{ mA}) (300 \text{ sec}) - (50.0 \text{ mA}) (100 \text{ sec}) = 10.0 \text{ coul}$$

$$\text{wt Br}_2, \text{ g} = \frac{10.0 \text{ coul}}{96,485 \text{ coul/eq}} \times \frac{79.9 \text{ g}}{\text{eq}} \times 10^4 = 82.8 \text{ g}$$

(Bromine no. is the weight of Br_2 that reacts with 100 g sample.)

3. Assume the acid is 100% titrated at pH 6.



$$\text{Total equivalents} = \frac{(15.0 \text{ mA}) (320 \text{ sec})}{\text{F}} = 4.97 \times 10^{-5}$$

Since 20.0 ml of the added acid contains this number of equivalents, the normality of the acid is

$$\left(\frac{1000}{20.0} \right) (4.97 \times 10^{-5}) = 2.49 \times 10^{-3} \text{ N}$$

M.W. AgBr = 187.80; wt. formed = 9.34×10^{-3} g

At STP, 1 mol of ideal gas has volume 22.414 l. 1 mol H_2 = 2 eq.
 $\frac{4.97 \times 10^{-5}}{2}(22,414 \text{ ml}) = 0.558 \text{ ml } H_2$

4. From Eqn. 4.21, we have:

$$\text{moles} = it/nF$$

$$\text{But equivalents} = \text{moles}/n = it/F = (\text{amps}) (\text{sec})/F$$

$$\mu \text{eq} = (\text{amps}) (\text{sec}) (10^6)/F$$

$$\mu \text{eq/sec} = 1.00000 (\text{amps}) (10^6)/96,485 = (\text{amps}) (10.364_3)$$

$$(\text{amps}) = 1.000/10.364_3 = 0.096485 \text{ A} = 96.485 \text{ mA}$$

5. The normality equals the flow rate in ml/sec and from Faraday's law, the equivalents needed per second is given by

$$(\frac{i}{F}) = (N \frac{\text{eq}}{1}) (\frac{\text{ml}}{\text{sec}}) (10^{-3} \frac{\text{l}}{\text{ml}}) = 10^{-3} \phi^2$$

$$i = 10^{-3} \phi^2 F$$

where ϕ = flow rate in ml/sec

6. $N (\frac{\text{eq}}{\text{l}}) \nu (\text{ml/sec}) (0.001 \text{ l/ml}) (96,485 \text{ coul/eq}) = i \text{ coul/sec}$

$$N = \frac{1000i}{96,485 \nu} \text{ eq/l} = 1.036 \times 10^{-2} i/\nu (\text{eq/l})$$

7. g. of Ag = $\frac{(A.W.)Q}{nF} = \frac{107.868 \times 0.600}{1 \times 96,485} = 6.717 \times 10^{-4}$

$$\text{Volume of Ag} = \frac{6.717 \times 10^{-4} \text{ g}}{10.50 \text{ g/cm}^2} = 6.39 \times 10^{-5} \text{ cm}^3$$

$$\text{Area of electrode} = \pi r^2 = \pi \times (0.25 \text{ cm})^2 = 0.19_6 \text{ cm}^2$$

$$\text{Volume of Ag} = Ah = 6.39 \times 10^{-5} \text{ cm}^3$$

$$h = 6.39 \times 10^{-5} \text{ cm}^3 / 0.196 \text{ cm}^2 = 3.3 \times 10^{-4} \text{ cm} = 3.3 \mu\text{m}$$

$$8. \quad i_t = i_0 e^{-pt}$$

$$2.303 \log \frac{i_0}{i_t} = pt$$

$$p = 0.693/t_{\frac{1}{2}}$$

$$t/t_{\frac{1}{2}} = \frac{2.303}{0.693} \log i_0/i_t$$

$$\text{For 0.5 fraction deposited, } (1 - i_t/i_0) = 0.5$$

$$1 - i_t/i_0 = 0.5$$

$$-i_t/i_0 = 0.5 - 1 = -0.5$$

$$\log i_t/i_0 = -0.3010$$

$$\log i_0/i_t = 0.3010$$

$$t/t_{\frac{1}{2}} = \frac{2.303}{0.693} (0.3010) = 1.0$$

$(1 - i_t/i_0)$	$t/t_{\frac{1}{2}}$
0.50	1.0
0.90	3.3
0.99	6.7
0.999	10.0
0.9999	13.3

$$9. (a) p = Am/V = \frac{160 \times 0.00800}{75.0} = 0.0171 \text{ sec}^{-1}$$

$$t_{\frac{1}{2}} = \frac{0.693}{0.0171} = 40.5 \text{ sec}$$

$$t_{99.9} = 10 t_{\frac{1}{2}} = 405 \text{ sec}$$

9. (b) Using Eqn. 4.23, $i_t = i_0 e^{-pt}$, for thin layer cells, and rearranging,

$$t = \ln(i_0/i_t)/p$$

where

$$p = \pi^2 D / 4 l^2$$

$$= \pi^2 (1.00 \times 10^{-5} \text{ cm}^2/\text{sec}) / 4 (50 \times 10^{-4} \text{ cm})^2$$

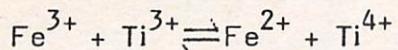
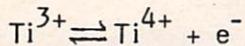
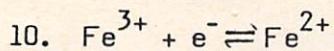
$$= 0.987$$

For 99.9% electrolysis, $i_t = 0.001 i_0$

$$\therefore t_{99.9\%} = \ln(i_0/0.001 i_0)/0.987 \text{ sec}^{-1}$$

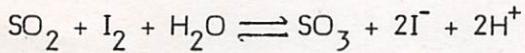
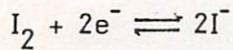
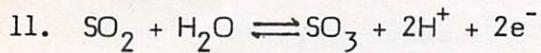
$$= \ln(1000)/0.987 \text{ sec}^{-1}$$

$$= 7.0 \text{ sec}$$



$$g_{\text{Fe}} = \frac{(\text{A.W.})it}{nF} = \frac{55.847 \times 1.567 \times 10^{-3} \times 123.0}{1 \times 96,485} = 1.115_6 \times 10^{-4}$$

$$\% \text{Fe} = \frac{1.115_6 \times 10^{-4} \times 100\%}{0.1000} = 0.1116\%$$



$$t = 10 \text{ min} = 10 \times 60 = 600 \text{ sec}$$

$$\text{eq}_{\text{SO}_2} = it/F = \frac{0.00140 \times 600}{96,485} = 8.71 \times 10^{-6}$$

$$\text{moles}_{\text{SO}_2} = 8.71 \times 10^{-6}/2 = 4.36 \times 10^{-6}$$

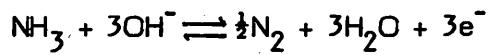
$$g_{\text{SO}_2} = 64.06 \times 4.36 \times 10^{-6} = 279 \times 10^{-6}$$

$$\mu\text{g}_{\text{SO}_2} = 279$$

$$\text{g of air passed} = 5.0 \text{ l/min} \times 10 \text{ min} \times 1.2 \text{ g/l} = 60 \text{ g}$$

$$\text{ppm}_{\text{SO}_2} = \frac{279 \mu\text{g of SO}_2}{60 \text{ g of air}} = 4.6_5$$

12. moles N = moles NH₃



$$\text{moles NH}_3 = \frac{it}{nF} = \frac{0.01000 \times 159.2}{96,485 \times 3} = 5.500 \text{ g} \times 10^{-6} \text{ in a 1.000 ml aliquot}$$

In 100.0 ml of sample,

$$\text{moles NH}_3 = \text{moles N} = 5.500 \text{ g} \times 10^{-6} \times 100.0 = 5.500 \text{ g} \times 10^{-4}$$

$$\text{g N} = 5.500 \times 10^{-4} \times 14.0067 = 0.007784$$

$$\text{mg N} = 7.704$$

CHAPTER 5

1. Given: $A = 1 \text{ cm}^2$
 $l = 0.25 \text{ cm}$
 $R = 274,700, 91,000, \text{ and } 18,320 \text{ ohms}$

Solution

$$\text{Cell constant } K = l/A = \frac{0.25}{1} = 0.25 \text{ cm}^{-1}$$

$$\text{Concentration } C = \frac{1000 K}{R \Lambda}$$

$\Lambda = \lambda_{\text{Na}^+} + \lambda_{\text{OAc}^-}$: Assume λ_{Na^+} and λ_{OAc^-} are equal to $\lambda^\circ_{\text{Na}^+}$ and $\lambda^\circ_{\text{OAc}^-}$ for the dilute solutions.

$$\Lambda = 50.1 + 40.9 = 91.0$$

$$1) C = \frac{1000 \times 0.25}{91.0 \times R} = \frac{250}{91 \times 274,700} = 0.000010 \underline{N}$$

$$2) C = \frac{250}{91 \times 91,000} = 0.000030 \underline{N}$$

$$3) C = \frac{250}{91 \times 18,320} = 0.00015 \underline{N}$$

2. This question is designed to test whether the student has a good grasp of the subject of conductivity. One of the concepts that must be realized is that in the question the two salts are on a molar basis. Since problems should be worked out on the basis of equivalents or normality, handling of the MgCl_2 on a molar basis can pose a problem. All λ° s given in the table are for equivalent conditions: thus Mg^{2+} accounts for only 1/2 the

concentration of Mg^{2+} . If an ion has 3 charges, then the equivalent conductance accounts for $1/3$ of the M^{3+} or X^{3-} species.

Solution

Given: $K = 5$; $R = 1549$ ohms; molar concentration of $NaCl$ = molar concentration of $MgCl_2$

Equations to be used:

$$\Lambda^{\circ}_{MX} = \Lambda^{\circ}_{M^+} + \Lambda^{\circ}_{X^-}$$

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$$

$$R = \frac{1000 K}{\Lambda C} \text{ or}$$

$$\frac{1}{R} = \frac{\Lambda C}{1000 K}$$

$$\text{Thus: } \frac{1}{R \text{ soln}} = \frac{\Lambda MgCl_2 \times C}{1000 K} + \frac{\Lambda NaCl \times C}{1000 K}$$

$$\frac{1}{1549} = \frac{2(\Lambda_{Mg^{2+}} + \Lambda_{Cl^-}) C}{1000 \times 5.000} + \frac{(\Lambda_{Na^+} + \Lambda_{Cl^-}) C}{1000 \times 5.000}$$

$$0.0006456 = \frac{2C (129.5)}{5000} + \frac{C (126.5)}{5000}$$

$$3.228 = 259.0 C + 126.5 C$$

$$3.228 = 385.5 C$$

$$0.008374 = C \text{ in normality of one } Cl^-$$

Substituting back to determine total chloride content:

$$Cl^- \text{ from } NaCl = 0.008374 \text{ gm. eq.}$$

$$Cl^- \text{ from } MgCl_2 = 2 \times 0.008374 \text{ or } 0.01675 \text{ gm. eq.}$$

Sum Cl^- = 0.02512 gm. eq.

A.W. of Cl^- = 35.45 g

Concentration = 0.02512 gm. eq./l \times 35.45 gm/gm. eq.

Concentration = 0.8905 gm/l

Concentration = 890.5 mg/l = ppm

One could take a shorter route and simply sum all equivalent conductances:

$$\lambda_{\text{MgCl}_2} = 2\lambda_{\text{I/2Mg}^{2+}} + 2\lambda_{\text{Cl}^-} = 2 \times 53.1 + 2 \times 76.4 = 259.0$$

$$\lambda_{\text{NaCl}} = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} = 50.1 + 76.4 = 126.5$$

$$\Lambda_{\text{soln}} = 385.5$$

$$C = \frac{1000 \times 5.000}{385.5 \times 1549} = 0.008373 \text{ N per Cl}^-$$

Since 3 Cl^- are involved, total $C_{\text{Cl}^-} = 3 \times 0.008373$ or 0.02512 and

$$\text{mg/l} = 0.02512 \times 35.45 \times 100 = 890.5 \text{ ppm Cl}^-$$

As a check, work the problem backward, starting with 890 ppm Cl^- , and see if you get a resistance value of ~ 1550 ohms.

3. Given: Ranges of bridge = 1000, 10,000, and 100,000 micromhos, or in mhos: 0.001, 0.01, and 0.1, respectively.

Mid-scale range (best working range) = 100, 1000, and 10,000 μ mhos. Select cell constant closest to one of above.

Cell constants available = 0.01, 1.0, and $25 \text{ cm}^{-1} = K$

Concentrations: 2.5 to 4.0 N NaOH

Equivalent conductances: 117 and 85, respectively.

Solution

a) Test concentrations and equivalent conductance for K and R.

Test for Specific Conductance

$$K = \frac{\Lambda C}{1000} = \frac{117 \times 2.5}{1000} = 0.29 \text{ mhos cm}^{-1} \text{ for } 2.5 \text{ N}$$

$$= \frac{85 \times 4.0}{1000} = 0.34 \text{ mhos cm}^{-1} \text{ for } 4.0 \text{ N}$$

Test for Effect of Cell Constant

$$1/R = K/K \text{ mhos.}$$

For 2.5 N: $\frac{0.29}{0.01} = 29 \text{ mhos}$

$$\frac{0.29}{1.0} = 0.29 \text{ mhos}$$

$$\frac{0.29}{25} = 0.012 \text{ mhos}$$

For 4.0 N: $\frac{0.34}{0.01} = 34 \text{ mhos}$

$$\frac{0.34}{1.0} = 0.34 \text{ mhos}$$

$$\frac{0.34}{25} = 0.014 \text{ mhos}$$

Mid-point of scales are: 0.0001, 0.001, and 0.01 mhos. Since a cell constant of 25 gives results closest to 0.01 mhos (0.012 and 0.014 mhos), K should be 25 cm^{-1} .

b) Based on results above, a 2.5 N solution with a cell constant of 25 cm^{-1} gives a resistance of 85 ohms, or a conductance of 0.012 mhos (12,000 micromhos). This is closest to mid-point of 100,000 micromho scale, therefore the 100,000 μmho scale should be used.

4. Given: K = 50

Concentration = 1 to 12 wt% H_2SO_4 , Temp = 18°C

$$1 \text{ wt\% H}_2\text{SO}_4 = 10 \text{ g H}_2\text{SO}_4 \text{ per liter} = \frac{10}{49} = 0.205 \text{ N}$$

$$12 \text{ wt\% H}_2\text{SO}_4 = 130 \text{ g/l} = 1.33 \text{ M} = 2.65 \text{ N}$$

Λ for 1 wt% ≈ 216

Λ for 12 wt% ≈ 172 (get from critical tables or handbooks - may have to interpolate)

$$\text{From } R = \frac{1000 \times K}{\Lambda \times C}$$

$$\text{Ans. for 12\% solution: } R = \frac{1000 \times 50}{172 \times 2.64} = 110 \text{ ohms}$$

$$\text{Ans. for 1\% solution: } R = \frac{1000 \times 50}{216 \times 0.205} = 1130 \text{ ohms}$$

$$\text{Ans. for 1\% solution: } 1/R = \frac{1}{1130} = 0.0000885 \text{ mhos or } 885 \mu\text{mhos}$$

$$\text{Ans. for 12\% solution: } 1/R = \frac{1}{110} = 0.00909 \text{ mhos or } 9090 \mu\text{mhos}$$

Note: The Critical Tables, the Rubber Handbook of Chemistry, or other sources of information must be used to obtain the correct information. The λ^0 values should not be used, since we are not working with dilute solutions. Result within $\pm 10\%$ is acceptable.

5. Given: $K = 0.150$

$$R = 1114 \text{ ohms}$$

$$2.4425 \text{ g. benzoic acid/liter}$$

Calculate Λ , α , and K_a

Assume limiting equivalent conductances can be used.

Solution

$$\text{M.W.} = 122.13$$

$$\text{Concentration} = \frac{2.4425}{122.13} = 0.02000 \text{ N}$$

$$\lambda^{\circ}_{H^+} = 349.8; \lambda^{\circ}_{A^-} = 32.4$$

Let A^- = Benzoate ion



$$\Lambda^{\circ} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{A^-} = 349.8 + 32.4 = 382.2$$

$$a) \text{ Actual } \Lambda = \frac{1000 \text{ K}}{C \times R} = \frac{0.150 \times 1000}{0.0200 \times 1114} = 6.73$$

$$b) \text{ Degree of dissociation: } \alpha = \frac{\Lambda}{\Lambda^{\circ}} = \frac{6.73}{382.2} = 0.0176$$

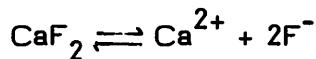
$$c) K_a = \frac{[C_{H^+}][C_{A^-}]}{[C_{HA}]} = \frac{(0.0200 \times 0.0176)(0.0200 \times 0.0176)}{(0.0200 \times 0.9824)}$$

$$K_a = 6.31 \times 10^{-6}$$

6. Given: $K_{sp} = 3.9 \times 10^{-11}$ for CaF_2

$$K = 0.100$$

Solution



$$K_{sp} = (\text{Ca}^{2+})(2\text{F}^-)^2$$

$$\text{or } 3.9 \times 10^{-11} = [X][2X]^2 = 4X^3$$

$$X = 2.14 \times 10^{-4} \text{ N}$$

$$\lambda^{\circ}_{\frac{1}{2}\text{Ca}^{2+}} = 59.5$$

$$\lambda^{\circ}_{\text{F}^-} = 55.4$$

$$\Lambda^{\circ} = (2 \times 59.5) + (2 \times 55.4) = 119.0 + 110.8 = 229.8$$

$$R = \frac{1000 \times 0.100}{229.8 \times 0.000214} = 2030 \text{ ohms}$$

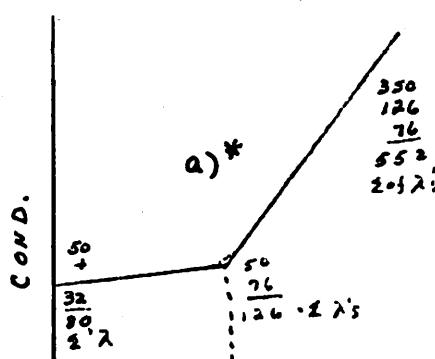
7. Plot ml. titrant vs. conductance reading and draw straight lines before and after end

points, ignoring points near end point. Where lines cross, indicate end point.

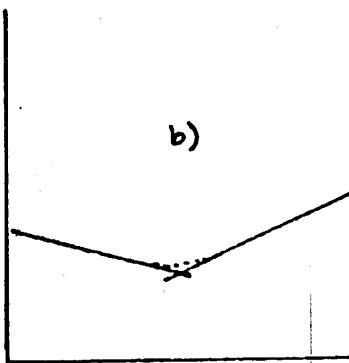
End pt. \approx 1.75 ml of 1 N NaOH

$$\underline{N} \text{ of NaOH} = \frac{1 \times 1.75}{100} = 0.0175 \underline{N} \text{ HOAc}$$

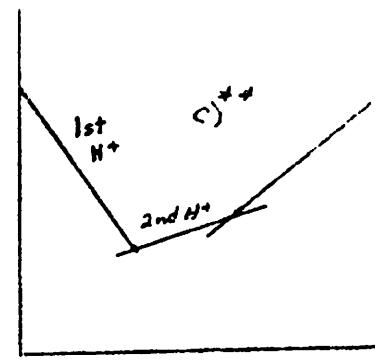
8. Use λ° for setting up general shape of curves.



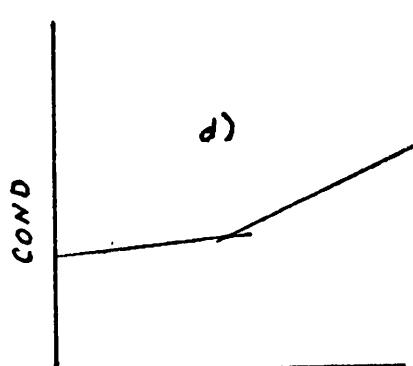
VOL. TITRANT
NaBr with HCl



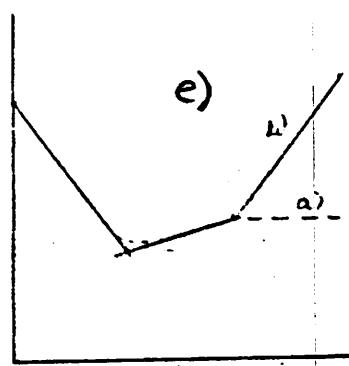
VOL. TITRANT
AgOAc with LiCl



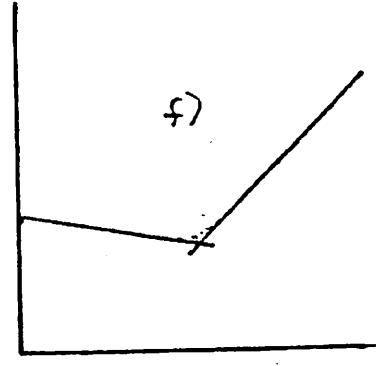
VOL. TITRANT
 H_2SO_4 in
Glacial HOAc with NaOH



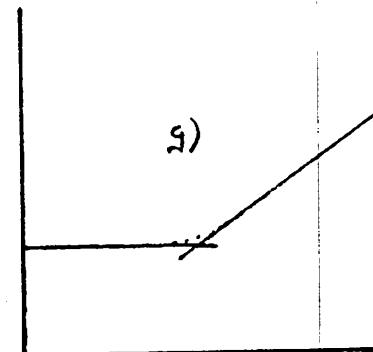
VOL. TITRANT
 $HgNO_3$ with KCl



VOL. TITRANT
HCl & HOAc with
a) NH_4OH b) NaOH



VOL. TITRANT
 NH_4Cl with KOH



VOL. TITRANT
 Na_2CO_3 with $Ca(NO_3)_2$

*Shows summing of λ 's at 1) beginning, 2) end pt., 3) 100% excess

** H_2SO_4 in glacial HOAc is ionized mainly as $H^+ + HSO_4^-$ (1st end pt.),
then $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ + NaOH $\rightleftharpoons Na^+ + SO_4^{2-} + H_2O$ at 2nd end pt.
Assume Na^+ of HSO_4^- about same as SO_4^{2-} .

9. Given: $K_{H_2O} = 0.81 \times 10^{-6}$ mho cm^{-1}

$$K_{\text{soln}} = 2.62 \times 10^{-6}$$
 mho cm^{-1}

$$\Lambda_{\text{AgCl}} = 138.3 \text{ cm}^2 \text{ mho eq.}$$

Temp = 25°C

Solution

$$\Lambda = \frac{1000}{C} \text{ or } C = \frac{1000 \Lambda}{K}$$

$$K_{\text{sp}} = [\text{Ag}^+] [\text{Cl}^-]$$

$$K_{\text{AgCl}} = K_{\text{soln}} - K_{H_2O}$$

$$K_{\text{AgCl}} = (2.62 - 0.81) \times 10^{-6} = 1.81 \times 10^{-6}$$

$$C = \frac{1000 \times 1.81 \times 10^{-6}}{138.3} = 0.0000131 \text{ N}$$

$$K_{\text{sp}} (\text{AgCl}) = [1.31 \times 10^{-5}]^2 = 1.72 \times 10^{-10}$$

10. Plotting the oscilloscope readings as a function of the percent glycerol, first for 0-5% glycerol and second for 95-100% glycerol, results in slightly curved calibration curves. The first gives a value of 1.5% glycerol for a reading of 371, and the second gives a value of 97.6% glycerol for a reading of 1,361. Hence, the hydrocarbon layer contains 1.5% glycerol and the glycerol layer contains $100.0 - 97.6 = 2.4\%$ hydrocarbon.

11. Substance Titrated	Reagent	Concentration Range	Special Conditions
---------------------------	---------	------------------------	--------------------

Ag ⁺	NaCl or LiCl	$10^{-1} - 10^{-4}$ M	Neutral solution, add EtOH for very dilute solutions.
-----------------	--------------	-----------------------	---

Ba ²⁺	Li ₂ SO ₄ or Li ₂ CrO ₄	$10^{-1} - 10^{-3}$ M	Use 30 to 40% EtOH. Wait a few minutes after each addition for ppt. to form.
------------------	--	-----------------------	---

Br^-	AgNO_3	$10^{-1} - 10^{-5} \text{M}$	Neutral solution, add EtOH for very dilute solutions.
CN^-	AgNO_3	$10^{-1} - 10^{-3} \text{M}$	Neutral solution. 2 breaks in titrn curve. 2nd break due to $\text{Ag}(\text{CN})_2^-$ and is best to use.
CO_3^{2-}	HCl	$10^{-2} - 10^{-4} \text{M}$	Two breaks, three if OH^- is present.
Cd^{2+}	EDTA or 10^{-3}M H_2S (aq.)	10^{-1}M $10^{-4} - 10^{-6} \text{M}$	Buffer, OAc^- , pH of 5.
Cl^-	AgNO_3	$10^{-1} - 10^{-5} \text{M}$	Use 90% EtOH for very dilute solutions
SCN^-	AgNO_3	$10^{-1} - 10^{-5} \text{M}$	Neutral or sl. acid soln; use EtOH for very dilute solutions.
SO_4^{2-}	$\text{Ba}(\text{OAc})_2$ in 1% HOAc	$10^{-1} - 10^{-4} \text{M}$	Use 20-30% EtOH, large amts. of NO_3^- interfere.
Zn^{2+}	EDTA or NaOH	10^{-2}M $10^{-2} - 10^{-3} \text{M}$	Same as for Cd^{2+} Two end points if soln. contains H^+ equiv. to Zn^{2+} , 1st for neut. and 2nd for pptn. of $\text{Zn}(\text{OH})_2$

12. a) GC with HECD
 b) Conductometric with alcoholic NH_4OH or by oscilloscopy
 c) Water bubbler sampler and ion chromatography with micro-cell
 d) Oscillosmeter
 e) Base titration by conductometry and GC-HECD after dilution

f) Both ion and gas chromatography with micro-cell and HECD detectors, respectively.

13. At. wt. HF = 20; at. wt. CO₂ = 44

$$\text{g HF/1000 ml gas} = 5 \times 10^{-6} \times (44/22.4) = 9.82 \times 10^{-6} \text{ g}$$

$$\text{Temp. correction: } 273/298 \times 9.82 \times 10^{-6} = 9.00 \times 10^{-6} \text{ g}$$

$$\text{Normality: } 9.00 \times 10^{-6}/20 = 0.45 \times 10^{-6} \text{ g/10 ml} = 0.45 \times 10^{-4} \text{ mole/liter} = \underline{N}$$

$$\text{Conductivity correction: } \lambda^0 \text{HF} (350 + 55)/\lambda^0 \text{HCO}_3 (350 + 44.5) = 1.027$$

$$\text{Conductivity equivalent conc. HCO}_3^- = 1.027 \times 0.45 \times 10^{-4} = 0.462 \times 10^{-4} \underline{N}$$

$$\text{H}_2\text{CO}_3 = (0.462 \times 10^{-4})^2/4.4 \times 10^{-7} = 4.85 \times 10^{-3} \text{ mole/liter}$$

$$\text{Solubility CO}_2 \text{ with temp. correction} = (958/22400) \times (273.298) = 0.0392$$

mole/liter

Since solubility is proportional to partial pressure, the volume percentage of

$$\text{CO}_2 = 0.00485/0.0392 = 0.124 \text{ mol fraction or 12.4 vol. \%}$$

CHAPTER 6

1. a) From Eqn. 6.1, $\lambda = 1/\bar{\nu}$

$$\lambda = 1/2000 \text{ cm}^{-1} = 5.000 \times 10^{-4} \text{ cm} = 5.000 \mu\text{m}$$

b) Using the conversion factors in Table 6.1, $2000 \text{ cm}^{-1} (1.240 \times 10^{-4} \frac{\text{eV/molecule}}{\text{cm}^{-1}})$

$$= 0.2480 \text{ eV/molecule}$$

c) $2000 \text{ cm}^{-1} (2.8591 \frac{\text{cal/mole}}{\text{cm}^{-1}}) = 5718 \text{ cal/mole}$

d) $2000 \text{ cm}^{-1} (1.986 \times 10^{-16} \frac{\text{ergs/molecule}}{\text{cm}^{-1}}) = 3.972 \times 10^{-13} \text{ ergs/molecule}$

2. a) From Eqn. 6.1, $\bar{\nu} = 1/\lambda$

$$\bar{\nu} = \frac{1}{4.50 \mu\text{m} (10^{-4} \text{ cm}/\mu\text{m})} = 2.22 \times 10^3 \text{ cm}^{-1}$$

b) From Eqn. 6.1, $\nu = c/\lambda$, where c is the velocity of light.

$$\nu = \frac{2.9979 \times 10^{10} \text{ cm/sec}}{4.5 \times 10^{-4} \text{ cm}} = 6.66 \times 10^{13} \text{ sec}^{-1} \text{ or Hz}$$

c) $4.50 \mu\text{m} (10^{-6} \text{ m}/\mu\text{m}) (10^{10} \text{ \AA/m}) = 4.50 \times 10^4 \text{ \AA}$

d) Using the conversion factors in Table 6.1, and the fact that $\bar{\nu} = 2.22 \times 10^3 \text{ cm}^{-1}$:

$$2.22 \times 10^3 \text{ cm}^{-1} (1.986 \times 10^{-16} \frac{\text{ergs/molecule}}{\text{cm}^{-1}}) = 4.41 \times 10^{-13} \text{ ergs/molecule}$$

e) $2.22 \times 10^3 \text{ cm}^{-1} (1.240 \times 10^{-4} \frac{\text{eV/molecule}}{\text{cm}^{-1}}) = 0.275 \text{ eV/molecule}$

3. a) From Eqn. 6.1, $\nu = c/\lambda$

$$\nu = \frac{2.9979 \times 10^{10} \text{ cm/sec}}{500 \mu\text{m} (10^{-4} \text{ cm}/\mu\text{m})} = 6.00 \times 10^{11} \text{ Hz}$$

$$\text{b) } \bar{\nu} = 1/\lambda = \frac{1}{500 \mu\text{m} (10^{-4} \text{ cm}/\mu\text{m})} = 20.0 \text{ cm}^{-1}$$

$$\text{c) } 20.0 \text{ cm}^{-1} (1.240 \times 10^{-4} \frac{\text{eV}/\text{molecule}}{\text{cm}^{-1}}) = 2.48 \times 10^{-3} \text{ eV}/\text{molecule}$$

$$\text{4. a) } \nu = c/\lambda = \frac{2.9979 \times 10^{10} \text{ cm/sec}}{5145 \text{ \AA}} (10^8 \text{ \AA}/\text{cm}) = 5.827 \times 10^{14} \text{ Hz}$$

$$\text{b) } \bar{\nu} = 1/\lambda = \frac{(10^8 \text{ \AA}/\text{cm})}{5145 \text{ \AA}} = 1.944 \times 10^4 \text{ cm}^{-1}$$

$$\text{c) } \frac{5145 \text{ \AA} (10^6 \mu\text{m}/\text{m})}{10^{10} \text{ \AA}/\text{m}} = 0.5145 \mu\text{m}$$

$$\text{d) } 5145 \text{ \AA} = 1.944 \times 10^4 \text{ cm}^{-1}$$

$$1.944 \times 10^4 \text{ cm}^{-1} (1.240 \times 10^{-4} \frac{\text{eV}/\text{molecule}}{\text{cm}^{-1}}) = 2.410 \text{ eV}/\text{molecule}$$

$$\text{or from Eqn. 6.4, } E = \frac{12399}{\lambda(\text{\AA})} = \frac{12399}{5145 \text{ \AA}} = 2.410 \text{ eV}/\text{molecule}$$

5. a) The resolution of a Fourier transform spectrometer is determined primarily by the reciprocal of the optical path difference; therefore,

$$\text{resolution} = \frac{1}{5 \text{ cm}} = 0.2 \text{ cm}^{-1}$$

$$\text{b) optical path difference} = 1/\text{resolution} = 1/0.2 \text{ cm}^{-1} = 5 \text{ cm}$$

6. a) If the grating is ruled at 20 lines/mm, the groove spacing $d = 1/20 \text{ mm} = 0.050 \text{ mm}$
Using Eqn. 6.8, and the fact that $\sin \theta = \sin i$

$$n\lambda = 2d \sin \theta$$

$$\sin \theta = \frac{n\lambda}{2d} = \frac{(1) (40 \mu\text{m}) (10^{-3} \text{ mm}/\mu\text{m})}{2(0.050 \text{ mm})} = 0.400$$

$$\theta = 23.6^\circ$$

b) From Fig. 6.1, $40 \mu\text{m}$ is in the infrared portion of the electromagnetic spectrum.
c) From Eqn. 6.8, the product n is a constant if d , $\sin i$, and $\sin \theta$ remain constant.
Therefore, the second-order wavelength would be one-half of $40 \mu\text{m}$, or $20 \mu\text{m}$.

7. a) From Eqn. 6.6,

$$\frac{\sin \phi_1}{\sin \phi'_1} = \frac{n'}{n}$$

$$\sin \phi'_1 = \frac{n \sin \phi_1}{n'} = \frac{1.00 (\sin 60^\circ)}{1.60} = 0.541$$

$$\phi'_1 = 32.8^\circ$$

b) If $\phi'_2 = 20.5^\circ$, from Eqn. 6.6,

$$\frac{n'}{n} = \frac{\sin \phi_2}{\sin \phi'_2}$$

$$\sin \phi_2 = \frac{n' \sin \phi'_2}{n} = \frac{1.60 (\sin 20.5^\circ)}{1.00} = 0.560$$

$$\phi_2 = 34.1^\circ$$

CHAPTER 7

$$1. \quad 5889.97 \text{ \AA} \times \frac{1 \text{ nm}}{10 \text{ \AA}} = \boxed{588.997 \text{ nm.}}$$

$$\lambda v = c$$

$$v = 2.99776 \times 10^{10} \frac{\text{cm}}{\text{sec.}} \times \frac{1}{5889.97 \text{ \AA}}$$

$$\times \frac{1 \text{ \AA}^{\circ}}{1.00 \times 10^{-8} \text{ cm.}} = 5.0896 \times 10^{14} \text{ sec}^{-1}$$

$$= \boxed{5.0896 \times 10^{14} \text{ Hz}}$$

$$2. \quad h\nu = 5.14 \text{ eV} - 3.62 \text{ eV} - 6.2 \text{ eV} = \boxed{-4.68 \text{ eV}}$$

The fact that $h\nu$ is negative tells us that the ground state is actually $\text{Na}^+ - \text{Cl}^-$ ($\text{Na}^{\delta+} - \text{Cl}^{\delta-}$) and that the charge transfer process involves transfer of an electron from the more electronegative Cl to electropositive Na.

Hence, the charge transfer process is $\text{Na}^+ - \text{Cl}^- \xrightarrow{h\nu} \text{NaCl}$

$$h\nu = 4.68 \text{ eV} \times \frac{8065.73 \text{ cm}^{-1}}{1.00 \text{ eV}} = 37748 \text{ cm}^{-1} = \frac{1}{\lambda}$$

$$\lambda = \frac{1}{37748 \text{ cm}^{-1}} \times \frac{1.00 \text{ \AA}^{\circ}}{1.00 \times 10^{-8} \text{ cm}} = \boxed{2650 \text{ \AA}^{\circ}}$$

$$3. \quad \frac{c_{\text{NaCl}}}{\frac{q_{\text{Na}^+} + q_{\text{Cl}^-}}{d_{\text{Na}^+ \text{Cl}^-}}} = \frac{c_{\text{KCl}}}{\frac{q_{\text{K}^+} + q_{\text{Cl}^-}}{d_{\text{K}^+ \text{Cl}^-}}}$$

$$\text{but } q_{\text{Na}^+} = q_{\text{K}^+}$$

$$\text{therefore } c_{\text{NaCl}} \cdot d_{\text{Na}^+ \text{Cl}^-} = c_{\text{KCl}} \cdot d_{\text{K}^+ \text{Cl}^-}$$

$$d_{\text{Na}^+ \text{Cl}^-} = r_{\text{Na}^+} + r_{\text{Cl}^-} = 2.78 \text{ \AA}^{\circ}$$

$$d_{\text{K}^+ \text{Cl}^-} = r_{\text{K}^+} + r_{\text{Cl}^-} = 3.14 \text{ \AA}^{\circ}$$

$$c_{\text{KCl}} = c_{\text{NaCl}} \frac{d_{\text{Na}^+ \text{Cl}^-}}{d_{\text{K}^+ \text{Cl}^-}} = 6.2 \text{ eV} \cdot \frac{2.78 \text{ \AA}^{\circ}}{3.14 \text{ \AA}}$$

$$= 5.5 \text{ eV}$$

$$h\nu = 4.34 \text{ eV} - 3.62 \text{ eV} - 5.5 \text{ eV} = \boxed{-4.78 \text{ eV}}$$

$$h\nu = 4.78 \text{ eV} \times \frac{8065.73 \text{ cm}^{-1}}{1.00 \text{ eV}} = 38554 \text{ cm}^{-1} = \frac{1}{\lambda}$$

$$\lambda = \frac{1}{38554 \text{ cm}^{-1}} \times \frac{1.00 \text{ }^{\circ}\text{A}}{1.00 \times 10^{-8} \text{ cm}} = 2590 \text{ }^{\circ}\text{A}$$

4. $\epsilon = 2.12 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$

$$A_{\min} = 0.001 \quad b = 10 \text{ cm.}$$

$$\text{then } C_{\min} = \frac{A_{\min}}{\epsilon b} = \frac{0.001}{2.12 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1} (10 \text{ cm})}$$

$$= \boxed{4.72 \times 10^{-10} \text{ M}}$$

$$4.72 \times 10^{-10} \frac{\text{moles}}{\text{L}} \times \frac{1.00 \text{ L}}{1000 \text{ ml}} \times 10 \text{ ml} \times \frac{106.4 \text{ g}}{\text{mole}}$$

$$\times \frac{10^9 \text{ nanograms}}{1.00 \text{ g}} = \boxed{0.502 \text{ nanograms}}$$

5. Assuming that the stability constant of complex formation is large or that X_0 is present in large excess, all of the Zr will be converted to complex.

$$\text{Then } [\text{Zr } X_0] = \frac{5.00 \times 10^{-7} \text{ mole}}{0.025 \text{ L}} = 2.00 \times 10^{-5} \text{ M}$$

$$A = 0.484 \quad b = 1.00 \text{ cm.}$$

$$\begin{aligned} \epsilon &= \frac{A}{bc} = \frac{0.484}{1.00 \text{ cm} (2.00 \times 10^{-5} \text{ M})} \\ &= \boxed{2.42 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}} \end{aligned}$$

6. $A_{285} = \epsilon(285)_{\text{o-NA}} b C_{\text{o-NA}} + \epsilon(285)_{\text{p-NA}} b C_{\text{p-NA}}$

$$0.321 = 5260 (1.00) C_{\text{o-NA}} + 1400 (1.00) C_{\text{p-NA}}$$

$$A_{347} = \epsilon(347)_{\text{o-NA}} b C_{\text{o-NA}} + \epsilon(347)_{\text{p-NA}} b C_{\text{p-NA}}$$

$$0.866 = 1280 (1.00) C_{\text{o-NA}} + 9200 (1.00) C_{\text{p-NA}}$$

we have two equations in two unknowns:

$$5260 C_{o-NA} + 1400 C_{p-NA} = 0.321$$

$$1280 C_{o-NA} + 9200 C_{p-NA} = 0.866$$

These equations can be solved simultaneously, by substitution, or by the method of determinants. We solve here by the method of determinants, since this is the most useful method when three or more unknowns are present.

The student should familiarize himself with this method.

$$C_{o-NA} = \frac{\begin{array}{cc} 0.321 & 1400 \\ 0.866 & 9200 \end{array}}{\begin{array}{cc} 5260 & 1400 \\ 1280 & 9200 \end{array}} = \frac{2953.2 - 1212.4}{4.84 \times 10^7 - 1.79 \times 10^6} = 3.73 \times 10^{-5} M$$

$$C_{p-NA} = \frac{\begin{array}{cc} 5260 & 0.321 \\ 1280 & 0.866 \end{array}}{\begin{array}{cc} 5260 & 1400 \\ 1280 & 9200 \end{array}} = \frac{4555.16 - 410.88}{4.84 \times 10^7 - 1.79 \times 10^6} = 8.89 \times 10^{-5} M$$

$$\text{moles } o\text{-NA} = 3.73 \times 10^{-5} \frac{\text{moles}}{\text{L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 100 \text{ mL}$$

$$\times \frac{12.000 \text{ gms}}{0.00175 \text{ gms}} = 2.56 \times 10^{-2} \text{ moles}$$

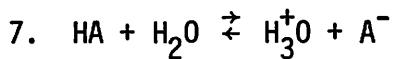
$$\text{moles aniline} = 10.00 \text{ gms.} \times \frac{1 \text{ mole}}{93 \text{ g}} = 0.108 \text{ moles}$$

$$\% \text{ yield } o\text{-NA} = \frac{2.56 \times 10^{-2} \text{ moles}}{0.108 \text{ moles}} \times 100 = \boxed{23.7\%}$$

$$\text{moles p-NA} = 8.89 \times 10^{-5} \frac{\text{moles}}{\ell} \times \frac{1 \ell}{1000 \text{ ml}} \times 100 \text{ ml}$$

$$\times \frac{12.000 \text{ gms}}{0.00175 \text{ gms}} = 6.10 \times 10^{-2} \text{ moles}$$

$$\% \text{ yield p-NA} = \frac{6.10 \times 10^{-2} \text{ moles}}{0.108 \text{ moles}} \times 100 = \boxed{56.4\%}$$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

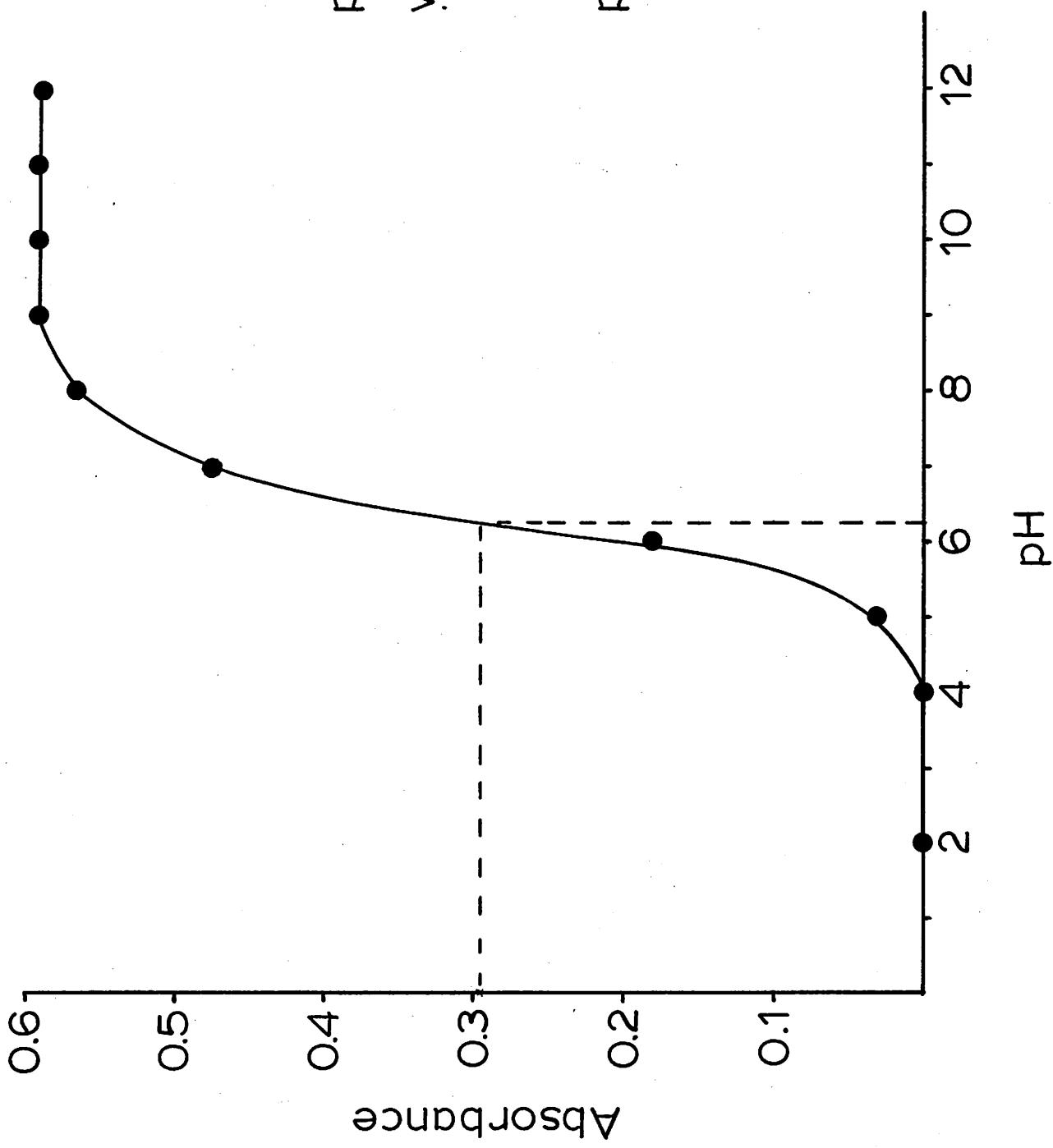
note that $K_a = [\text{H}_3\text{O}^+]$ when $[\text{A}^-] = [\text{HA}]$; $C_{\text{HA}} = [\text{HA}] + [\text{A}^-]$

at very low pH all acid is present as HA

at very high pH all acid is present as A^- and maximum absorbance is obtained

$$K_a = [\text{H}_3\text{O}^+] \text{ when } [\text{A}^-] = [\text{HA}] = 1/2 C_{\text{HA}}$$

at this point $\text{A}^- = 1/2$ maximum absorbance



8. $\frac{2.00 \text{ mg}}{\ell} \times A = 0.840 \quad b = 2.00 \text{ cm.}$

F.W. of X = 150

a) $c = \frac{2.00 \text{ mg}}{\ell} \times \frac{1 \text{ gm}}{1000 \text{ ml}} = 2.00 \times 10^{-3} \frac{\text{g}}{\ell}$

$$a = \frac{A}{bc} = \frac{0.840}{(2.00 \text{ cm})(2.00 \times 10^{-3} \text{ g/}\ell)}$$

$$= \boxed{2.10 \times 10^2 \text{ (g/}\ell)^{-1} \text{ cm}^{-1}}$$

b) $\epsilon = aM$

$$= 2.10 \times 10^2 \text{ (g/}\ell)^{-1} \text{ cm}^{-1} \times 150 \text{ g mole}^{-1}$$

$$= \boxed{3.15 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}}$$

c) $c = \frac{0.250}{(1.00 \text{ cm})(2.10 \times 10^2 \text{ (g/}\ell)^{-1} \text{ cm}^{-1})} = 1.18 \times 10^{-3} \text{ g/}\ell$

$$\text{wt. of X} = 1.19 \times 10^{-3} \frac{\text{g}}{\ell} \times 1000 \frac{\text{mg}}{\text{g}} \times \frac{1 \text{ }\ell}{1000 \text{ ml}} \times 25 \text{ ml}$$

$$= \boxed{0.0298 \text{ mg.}}$$

d) $1.19 \times 10^{-3} \frac{\text{g}}{\ell} \times 1000 \frac{\text{mg}}{\text{g}} \times \frac{1 \text{ ppm}}{\text{mg } \ell^{-1}}$

$$= \boxed{1.19 \text{ ppm}}$$

9. Known sample

$$c_{\text{Cu}} = \frac{0.500 \text{ g} \times 0.00240}{0.050 \text{ }\ell} = 0.0240 \frac{\text{g}}{\ell}$$

$$ab = \frac{A}{c} = \frac{0.600}{0.0240 \text{ g/}\ell} = 25 \text{ (g/}\ell)^{-1}$$

unknown sample:

$$c_{\text{Cu}} = \frac{A}{ab} = \frac{0.260}{25 \text{ (g/}\ell)^{-1}} = 0.0104 \frac{\text{g}}{\ell}$$

$$\text{gms of Cu} = 0.0104 \frac{\text{g}}{\ell} \times \frac{1 \text{ }\ell}{1000 \text{ ml}} \times 50.0 \text{ ml.}$$

$$= 0.000520 \text{ gms.}$$

$$\% \text{ Cu} = \frac{0.000520 \text{ g}}{0.2000 \text{ g}} \times 100 = \boxed{0.260\%}$$

$$10. A = 0.393 \quad b = 1.00 \text{ cm.} \quad \epsilon = 2025 \text{ M}^{-1} \text{ cm}^{-1}$$

$$C_{\text{Mn}} = \frac{A}{\epsilon b} = \frac{0.393}{(2025 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})}$$

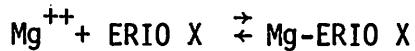
$$= 1.94 \times 10^{-4} \text{ M}$$

$$\text{wt. Mn} = 1.94 \times 10^{-4} \frac{\text{moles}}{\text{l}} \times \frac{1 \text{ l}}{1000 \text{ ml.}} \times 250.0 \text{ ml.} \times$$

$$54.938 \frac{\text{g}}{\text{mole}} = 2.66 \times 10^{-3} \text{ g}$$

$$\% \text{ Mn} = \frac{2.66 \times 10^{-3} \text{ g}}{0.500 \text{ g}} \times 100 = \boxed{0.533\%}$$

$$11. \text{ at equiv. pt. } [\text{Mg-ERIO X}] = [\text{ERIO X}] = 5 \times 10^{-7} \text{ M}$$



$$K_f = \frac{[\text{Mg-ERIO X}]}{[\text{Mg}^{++}][\text{ERIO X}]}$$

since at the equivalence point, a stoichiometric amount of Mg^{++} has been added $[\text{Mg}^{++}] = [\text{ERIO X}] = 5 \times 10^{-7} \text{ M}$

$$K_f = \frac{5 \times 10^{-7}}{(5 \times 10^{-7})^2} = \boxed{2.0 \times 10^6}$$

12. At the equivalence point

$$\text{moles base} = \text{moles acid}$$

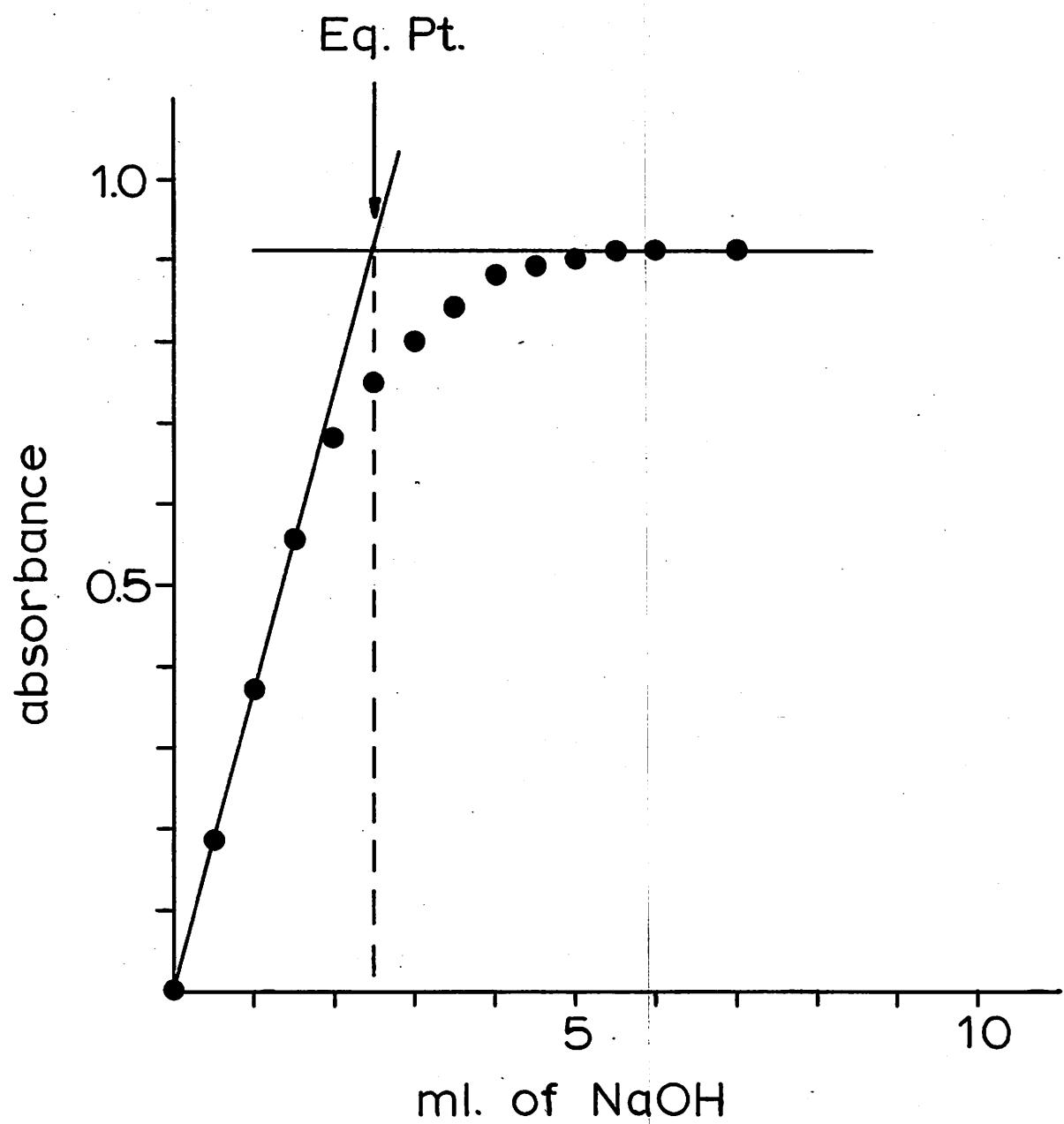
From graph, eq. pt is at 2.5 ml of NaOH

$$\text{moles acid} = 0.0500 \frac{\text{moles}}{\text{l}} \times 2.5 \text{ ml} \times \frac{1 \text{ l}}{1000 \text{ ml.}}$$

$$= 1.25 \times 10^{-4}$$

$$0.0150 \text{ g HA} = 1.25 \times 10^{-4} \text{ moles HA}$$

$$\text{Molecular wt.} = \frac{0.0150 \text{ g}}{1.25 \times 10^{-4} \text{ moles}} = \boxed{120 \text{ g/mole}}$$



7-46

13. a) From graph

$$\frac{[Bi]}{[Bi] + [X_0]} \approx 0.5 = \frac{1}{2}$$

Therefore the molar ratio of $[Bi]$ to $[X_0]$ is 1:1

b) The point at which the straight lines cross represent the absorbance if the complexation reaction occurred 100%. Then the extent of reaction is the ratio of the observed absorbance maximum to the theoretical absorbance for 100% reaction. If the concentration of the complex for 100% reaction is $[BiX_0]_0$.

Then at equil. $[BiX_0] = \alpha [BiX_0]_0$.

$$[Bi] = [X_0] = (1-\alpha) [BiX_0]_0$$

Then

$$K_f = \frac{[BiX_0]_0}{[Bi][X_0]} = \frac{\alpha [BiX_0]_0}{(1-\alpha)^2 [BiX_0]_0}$$
$$= \frac{\alpha}{(1-\alpha)^2 [BiX_0]_0}$$

For I:

$$[BiX_0]_0 = 1/2 (2.4 \times 10^{-5} M) = 1.2 \times 10^{-5} M$$

$$\text{from graph } \alpha = \frac{0.201}{0.250} = 0.804$$

$$K_f = \frac{0.804}{(1-0.804)^2 (1.2 \times 10^{-5})} = 1.74 \times 10^6$$

For II:

$$[BiX_0]_0 = 1/2 (3.2 \times 10^{-5}) = 1.6 \times 10^{-5} M$$

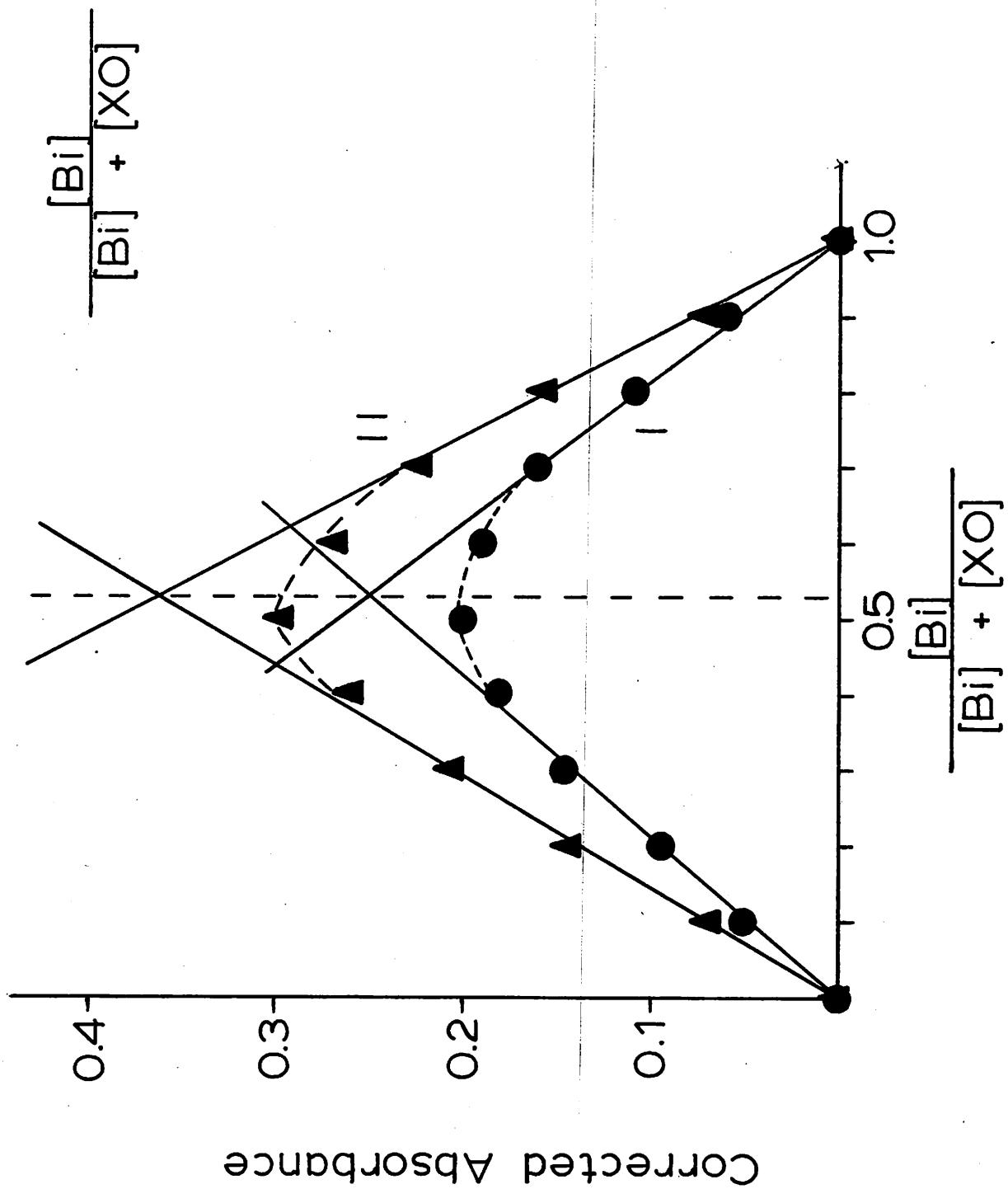
$$\text{from graph } \alpha = \frac{0.300}{0.360} = 0.833$$

$$K_f = \frac{0.833}{(1-0.833)^2 (1.6 \times 10^{-5})} = 1.87 \times 10^6$$

$$K_f \text{ average} = \boxed{1.8 \times 10^6}$$

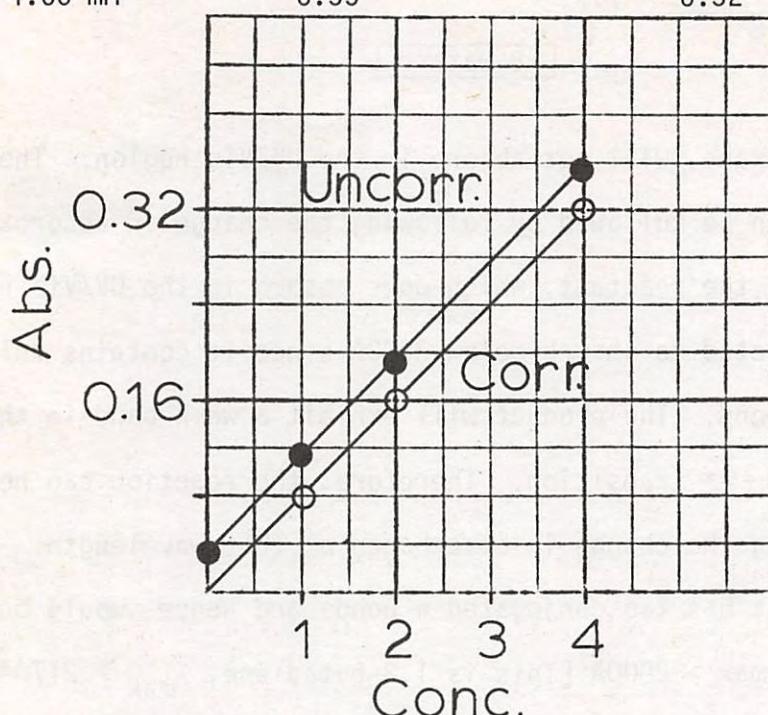
$\frac{1}{2}$

21



7-43

14. conc.	A	corr. A (A-A _{0.00})
0.00	0.03	0.00
1.00 mM	0.11	0.08
2.00 mM	0.19	0.16
4.00 mM	0.35	0.32



When the uncorrected data is plotted, the curve is linear but it does not pass through the origin as required by Beer's law. This can easily be corrected by correcting all absorbances by the blank absorbance.

15. a) Formula wt. of 5'-CMP = 367.2

$$C_{\text{nom}} = 0.0814 \text{ g} \times \frac{1 \text{ mole}}{367.2 \text{ g}} \times \frac{1}{0.025} = 0.00887 \text{ M}$$

b) Let C = conc. of solution in the cuvette

C_s = conc. of the stock solution according to spectrophotometry results

$$C = \frac{A}{\epsilon b} = \frac{0.831}{(13.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1})(0.992 \text{ cm})} \\ = 6.44 \times 10^{-5}$$

$$\frac{C_s(0.100)}{10.00} = 6.44 \times 10^{-5}$$

$$C_s = 0.00644 \text{ M}$$

c) Calculate the apparent formula weight

$$\text{F.W.'} = \frac{1}{0.00644 \text{ moles l}^{-1}} \times \frac{1}{0.02500 \text{ l}} \times 0.0814 \text{ g}$$
$$= 50.$$

$$\text{number of waters} = \frac{50 - 367.2}{18} = 7.7$$

\approx [8 waters]

16. a) The product, cyclohexane, will not absorb in the UV/Vis region. Therefore the reaction can be followed by following the change in absorbance with time for a λ of the reactant, which does absorb in the UV/Vis region.

b) The reactant is expected to absorb below 2000\AA since it contains only an isolated double bond. The product will exhibit a weak band in the UV region due to a $n \rightarrow \pi^*$ transition. Therefore, the reaction can be followed by following the change in absorbance at that wavelength.

c) The 4 carbon reactant has two conjugated π bonds and hence would be expected to give a $\lambda_{\text{max}} > 2000\text{\AA}$ [This is 1,3-butadiene, $\lambda_{\text{max}} = 2170\text{\AA}$ from text]. Ethylene and the product have only an isolated π bond and hence will not adsorb at $\lambda > 2000\text{\AA}$. Follow reaction at λ_{max} for 1,3-butadiene.

d) Formaldehyde exhibits a weak band in the UV due to a $n \rightarrow \pi^*$ transition. Neither product absorbs at $\lambda > 200\text{\AA}$. Follow reaction by monitoring absorbance of the reactant $n \rightarrow \pi^*$ band.

CHAPTER 8

1. a) $0.7\text{-}2.5 \mu\text{m}$; $2.5\text{-}50 \mu\text{m}$; $50\text{-}1000 \mu\text{m}$
 b) $14,285\text{-}4000 \text{ cm}^{-1}$; $4000\text{-}200 \text{ cm}^{-1}$; $200\text{-}10 \text{ cm}^{-1}$
2. a) $7000 \text{ \AA} = 7000 \times 10^{-9} \text{ cm} = 7000 \times 10^{-10} \text{ m}$

$$\frac{10^8 \text{ \AA}/\text{cm}}{7000 \text{ \AA}} = 14,285 \text{ cm}^{-1}$$

$$\text{b) } \frac{(7000 \times 10^{-10} \text{ m})}{(1 \times 10^{-6} \text{ m}/\mu\text{m})} = 7000 \times 10^{-4} \mu\text{m} = 0.7 \mu\text{m}$$

$$\text{c) } E = h\nu$$

$$= h \frac{c}{\lambda} = h \frac{3 \times 10^8 \text{ msec}^{-1}}{0.7 \times 10^{-6} \text{ m}}$$

$$= (6.6220 \text{ erg sec}) (4.2857 \times 10^{-14} \text{ sec}^{-1})$$

$$= (6.62620 \text{ erg sec}) (4.2857 \times 10^{-14} \text{ sec}^{-1})$$

$$= 28.3979 \times 10^{-13} \text{ erg}$$

$$= (28.3979 \times 10^{-13} \text{ erg}) (1 \text{ eV}/1.6021 \times 10^{-12} \text{ erg})$$

$$= 1.77 \text{ eV}$$

3. For methane ($N=5$) and benzene ($N=12$), there are $(3N-6)$ vibrations or $[3(5)-6] = 9$ and $[3(12)-6] = 30$, respectively. For the linear molecule acetylene, there are $3N-5$ or $[3(4)-5] = 7$ vibrations.

$$4. \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(12.0/6.02 \times 10^{23})(12.0/6.02 \times 10^{23})}{(12.0/6.02 \times 10^{23}) + (12.0/6.02 \times 10^{23})}$$

$$\mu = \frac{144/(6.02 \times 10^{23})^2}{24.0/(6.02 \times 10^{23})} = 6.00/(6.02 \times 10^{23})$$

$$\mu = 1.00 \times 10^{23} \text{ gm}$$

for C-C,

$$\begin{aligned}\bar{\nu} &= \frac{1}{2(3.14)(3.00 \times 10^{10})} \sqrt{\frac{1}{\mu}} \sqrt{k} \\ &= \frac{1}{18.8 \times 10^{10}} \sqrt{1.00 \times 10^{23}} \sqrt{k} \\ &= (1/18.8 \times 10^{10})(3.16 \times 10^{11}) \sqrt{k} \\ &= 0.168 \times 10^1 \sqrt{5 \times 10^5} = (1.67)(7.07 \times 10^2) \approx 1200 \text{ cm}^{-1}\end{aligned}$$

for C = C,

$$\bar{\nu} = 1.68 \sqrt{10 \times 10^5} = (1.68)(1.0 \times 10^3) \approx 1700 \text{ cm}^{-1}$$

for C \equiv C,

$$\bar{\nu} = 1.68 \sqrt{15 \times 10^5} = (1.68)(1.22 \times 10^3) \approx 2050 \text{ cm}^{-1}$$

$$\begin{aligned}5. \quad \bar{\nu}(\text{C-H}) &= 2900 \text{ cm}^{-1} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \\ \mu(\text{C-H}) &= \frac{(12.0)(1.01)}{(12.0 + 1.01)} \left(\frac{1}{6.02 \times 10^{23}} \right) = \frac{12.1}{13.0(6.02 \times 10^{23})} \\ \mu(\text{C-D}) &= \frac{24.2}{14.0(6.02 \times 10^{23})}\end{aligned}$$

We can assume a constant k for C-H and C-D, so

$$\begin{aligned}\bar{\nu}(\text{C-H}) &= 2900 \text{ cm}^{-1} = \frac{1}{2\pi c} \sqrt{k} \sqrt{\frac{1}{\mu}} \\ &= \frac{1}{2\pi c} \sqrt{k} \sqrt{\frac{13.0(6.02 \times 10^{23})}{12.1}} \\ \bar{\nu}(\text{C-D}) &= \frac{1}{2\pi c} \sqrt{k} \sqrt{\frac{14.0(6.02 \times 10^{23})}{24.2}}\end{aligned}$$

$$\bar{\nu}(\text{CH})/\bar{\nu}(\text{CD}) = \sqrt{\frac{13.0/12.1}{14.0/24.2}} = \sqrt{\frac{(13.0)(24.2)}{(12.1)(14.0)}} = 1.36$$

$$\bar{\nu}(\text{C-O}) = \bar{\nu}(\text{C-H})/1.36 = 2900 \text{ cm}^{-1}/1.36 \approx 2130 \text{ cm}^{-1}$$

6. For $514.5 \text{ nm} = 19436 \text{ cm}^{-1} = \bar{\nu}_L$

$$\bar{\nu}_S = \bar{\nu}_L - \bar{\nu}_1 = 19436 - 1730 = 17,706 \text{ cm}^{-1} = 564.8 \text{ nm}$$

$$\text{For } 496.5 \text{ nm, } \bar{\nu}_S = 20141 - 1730 = 18,411 \text{ cm}^{-1} = 543.2 \text{ nm}$$

$$\text{For } 488.0 \text{ nm, } \bar{\nu}_S = 20493 - 1730 = 18,762 \text{ cm}^{-1} = 533.0 \text{ nm}$$

$$\text{For } 457.9 \text{ nm, } \bar{\nu}_S = 21839 - 1730 = 20,109 \text{ cm}^{-1} = 497.3 \text{ nm}$$

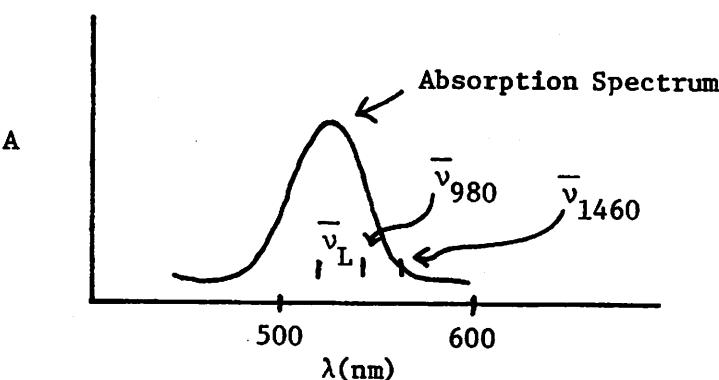
7. $k = 0.696 \text{ cm}^{-1} \text{ deg}^{-1}$ (see Chapter 6)

$$kT = 0.696 \text{ cm}^{-1} \text{ deg}^{-1} (300 \text{ deg}) = 209 \text{ cm}^{-1}$$

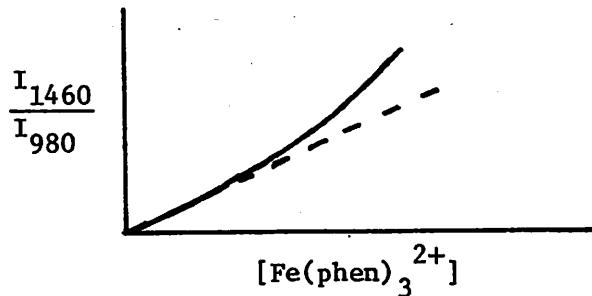
$$\frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} = \frac{N_u}{N_1} = e^{-(200 \text{ cm}^{-1}/209 \text{ cm}^{-1})} = e^{-0.957} = 0.384$$

Similarly, $N_u/N_1 = 0.0566$ and 0.00836 for 600 and 1000 cm^{-1} , respectively.

8.



The sulfate line occurs at 980 cm^{-1} and this is still within the absorption band of the complex, whereas the 1460 cm^{-1} band of the complex is no longer absorbed by the solution. As the complex concentration is increased, the sulfate band will be absorbed to a greater extent, but the band due to the complex will increase linearly.



9. $\rho = \frac{I_1}{I_2}$, so

$$\rho_{258} = 30.8/40.9 = 0.753 \text{ depolarized}$$

$$\rho_{357} = 5.8/78.2 = 0.074 \text{ polarized}$$

$$\rho_{660} = 1.3/83.2 = 0.016 \text{ polarized}$$

$$\rho_{760} = 4.7/6.0 = 0.78 \text{ depolarized}$$

10. The energy per pulse is given from Eqn. 8.8 as

$$\text{average power} = (\text{energy/pulse}) (\text{pulses/sec})$$

$$10 \text{ W} = X(20 \text{ pulses/sec})$$

$$\frac{(10 \text{ Joules sec}^{-1})}{20(\text{pulses sec}^{-1})} = X = 0.50 \text{ Joules/pulse}$$

The peak power is given from Eqn. 8.7 as

$$\text{peak power} = \frac{\text{Joules/pulse}}{\text{pulse width}}$$

$$(0.50 \text{ Joules pulse}^{-1}) / (10 \times 10^{-9} \text{ sec pulse}^{-1})$$

$$50 \times 10^6 \text{ watts} = 50 \text{ MW}$$

For the second case,

$$\text{energy/pulse} = 0.20 \text{ Joules/pulse}$$

$$\text{peak power} = 20 \text{ MW}$$

11. One should use AgCl windows in a sealed or demountable liquid cell of small path length. The use of CaF windows is not possible, since the transmission range is not large

enough. For those regions which are obscured, it may be helpful to use D₂O as the solvent in a second experiment.

CHAPTER 9

1. We will assume as in our discussion that electronic absorption of electromagnetic radiation must occur within one wave period of the exciting radiation. This means that the absorption must occur during the time of this one wave period. We can calculate that time using the wavelength of light (300nm or 3.00×10^{-5} cm) and the speed of light (3.00×10^{10} cm/sec). Consequently, the time of one wave period of 300nm light is

$$\text{time} = \frac{3.00 \times 10^{-5} \text{ cm}}{3.00 \times 10^{10} \text{ cm/sec}} = 1 \times 10^{-15} \text{ sec}$$

Thus, if our initial assumption is correct, absorption must occur in about 10^{-15} seconds.

2. By definition, an organic free radical has an odd electron, i.e., an unpaired electron. Recall that Equation 9.1 gives the molecular multiplicity, M, as.

$$M = 2S + 1.$$

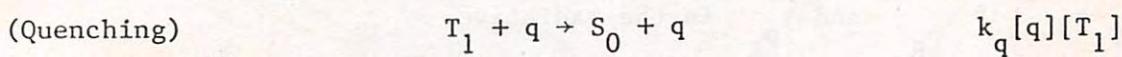
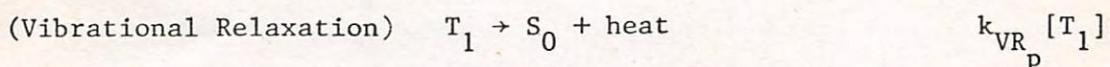
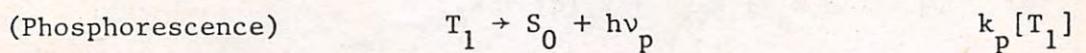
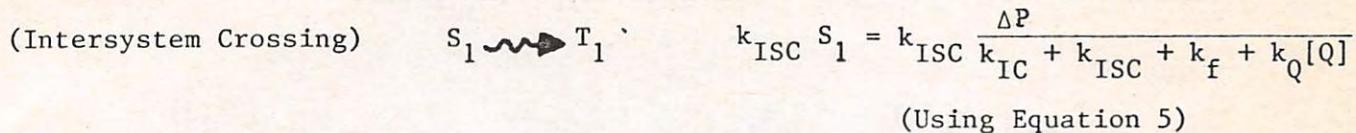
Since $S = 1/2$ for an organic radical,

$$M = 2 + 1/2 + 1 = 2.$$

Thus, an organic radical corresponds to a doublet state.

3. To answer this question, we must first define the processes which lead to and compete with phosphorescence.

Process



We define the triplet formation efficiency, ϕ_t , as

$$\phi_t = \frac{k_{ISC}}{k_{IC} + k_{ISC} + k_f + k_Q [Q]} \quad (1)$$

where these first order rate constants are as defined previously in Table 9.2. The rate constant k_p was also defined in Table 9.2. The other parameters, k_{VR_p} , $k_q [q]$ and k_d are, respectively, the rate constants for vibrational relaxation from T_1 , a pseudo first order rate constant for quenching by an impurity molecule, q and the rate constant for thermal activation of molecules in T_1 back to S_1 . As in our derivation of Equation 9.5 we can assume that the number of molecules in T_1 will reach a steady state, i.e.,

$$\phi_t \Delta P = (k_p + k_{VR_p} + k_q[q] + k_d) [T_1] . \quad (2)$$

Since the rate of phosphorescence is given by $k_p [T_1]$, we can define the overall phosphorescence efficiency, ϕ_p , as

$$\phi_p = \frac{k_p [T]}{\Delta I} = \frac{k_p \phi_t}{k_p + k_{VR_p} + k_q[q] + k_d} \quad (3)$$

where $k_p = 1 / \tau_{p_R}$ and τ_{p_R} is the radiative

lifetime of the triplet state. If one considers phosphorescence as well as competing processes, the true lifetime is given by

$$1 / \tau_p = k_p + k_{VR_p} + k_q[q] + k_d . \quad (4)$$

Thus, we can combine Equations (3) and (4) to obtain Equation 9.13 in the text

$$\frac{\phi_p}{\phi_t} = \frac{\tau_p}{\tau_{p_R}} .$$

4. For simplification of our discussion, we will assume that the transition moment of absorption of the fluorophore coincides with the transition moment of emission. This is a reasonably valid assumption if we have a rigid solution where the emission and absorption transitions are between the first excited singlet (S_1)

and the ground state (S_0). Thus, observation of the degree of polarization at right angles to the exciting light should give the maximum value of $P = +1/2$ (Equation 9.14) since there is no change of orientation between excitation and emission. However, consider the case where the solution has a low viscosity and the fluorescent molecules are allowed to rapidly rotate. If the lifetime of the excited state is long compared to this rotation, the molecules will have time to randomize before emission of fluorescence. Thus, the emitted fluorescence will not be polarized. It should be intuitively obvious that the degree of polarization will be directly related to the average time of rotation and thus the viscosity of the solvent as well as the lifetime of the fluorophore. It is also possible to use polarization to calculate the molar volume of the fluorophore. Further discussion is beyond this chapter, but additional details can be found in reference (8).

5. From Equation 9.15, we have

$$I_f = \Phi_f \Delta I = \Phi_f (I_0 - I_T) \quad 9.15$$

where the various terms are as defined in the text. Equation 9.16 is one form of Beer's law and gives us

$$I_T = I_0 10^{-\epsilon bc} \quad 9.16$$

substituting Equation 9.16 into Equation 9.15, we obtain

$$I_f = \phi_f (I_0 - I_0 10^{-\epsilon bc}) .$$

Factoring out I_0 , we obtain Equation 9.17

$$I_f = \phi_f I_0 (1 - 10^{-\epsilon bc}) . \quad 9.17$$

Using the relationship $10^{-x} = e^{-2.303x}$, we have

$$I_f = \phi_f I_0 (1 - e^{-2.303\epsilon bc}) .$$

We can use a Taylor expansion of the form

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots$$

where $x = -2.303\epsilon bc$ in this case to obtain

$$I_f = \phi_f I_0 \left[1 - (1 - 2.303\epsilon bc) + \frac{(2.303\epsilon bc)^2}{2!} + \frac{(2.303\epsilon bc)^3}{3!} + \dots \right]$$

At low absorbances ($\epsilon bc \leq 0.05$), the non-linear terms in ϵbc should be negligible (<5% error) and we have

$$I_f = \phi_f I_0 \left[1 - (1 - 2.303\epsilon bc) \right]$$

or

$$I_f = 2.303 \phi_f I_0 \epsilon bc .$$

6. Using Equation 9.8, we obtain the values of ϕ_f and ϕ_f° in the presence and absence of quencher molecules to be

$$\phi_f = \frac{k_f}{(k_{IC} + k_{ISC} + k_f + k_Q[Q])} \quad 9.8$$

and

$$\phi_f^\circ = \frac{k_f}{(k_{IC} + k_{ISC} + k_f)}$$

Taking the ratio of this latter equation and Equation 9.8, we obtain

$$\frac{\phi_f^\circ}{\phi_f} = \frac{(k_{IC} + k_{ISC} + k_f + k_Q[Q])}{(k_{IC} + k_{ISC} + k_f)}$$

and

$$\frac{\phi_f^\circ}{\phi_f} = 1 + \frac{k_Q[Q]}{(k_{IC} + k_{ISC} + k_p)}$$

We can define a new fluorescence lifetime, τ_0 , in the absence of quencher

$$\tau_0 = 1 / (k_{IC} + k_{ISC} + k_f)$$

and we have

$$\frac{\phi_f^\circ}{\phi_f} = k_Q \tau_0 [Q] + 1.$$

Therefore, the Stern-Volmer Constant, k_{SV} , is given by

$$k_{SV} = k_Q \tau_0$$

If we assume that I_0 and the absorbance remain the same in the presence and absence of the quencher (a reasonable assumption), it should be apparent that the Stern-Volmer equation can also be written in the form

$$\frac{I_f^\circ}{I_f} = k_Q \tau_0 [Q] + 1$$

If quenching occurs on each encounter of the fluorophore with a quencher molecule, then the reaction is diffusion controlled in liquid solutions. Thus, k_Q is then approximated by the bimolecular diffusion controlled rate constant, k_{dc} and we have

$$k_{SV} = k_{dc} \tau_0.$$

In typical aqueous and organic solutions (e.g. benzene), k_{dc} has a value of approximately 10^{10} liters/(mole·sec).

Static Quenching. A similar relationship exists for static quenching. Consider process II of Figure 9.10.



We can define the fraction α converted to FQ in the presence of a large excess of Q as

$$\alpha = \frac{[FQ]}{[F]_{\text{initial}}} .$$

If we assume that only static quenching occurs and that there is no "inner-filter" effect, then the observed intensity of fluorescence will be proportional to the concentration of uncomplexed F by a proportionality constant, β .

$$I_f = \beta (1 - \alpha) [F]_{\text{initial}}$$

and in the absence of quencher, Q, I_f° is given by

$$I_f^\circ = \beta [F]_{\text{initial}} .$$

Therefore,

$$\begin{aligned} I_f^\circ - I_f &= \beta [F]_{\text{initial}} - \beta [F]_{\text{initial}} + \beta \alpha [F]_{\text{initial}} \\ &= \beta \alpha [F]_{\text{initial}} \end{aligned}$$

and

$$\frac{I_f^* - I_f}{I_f} = \frac{\beta \alpha [F]_{\text{initial}}}{\beta (1 - \alpha) [F]_{\text{initial}}} = \frac{\alpha}{(1 - \alpha)} .$$

Since

$$K_{\text{eq}} = \frac{\alpha [F]_{\text{initial}}}{(1 - \alpha) [F]_{\text{initial}} [Q]} = \frac{\alpha}{(1 - \alpha) [Q]} ,$$

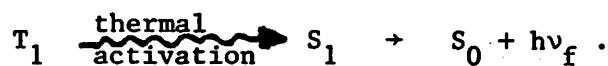
we have

$$\frac{I_f^*}{I_f} = K_{\text{eq}} [Q] + 1$$

which is identical in form to the Stern-Volmer relationship.

However, now k_{SV} is given by the equilibrium constant for formation of the complex, FQ .

7. Let us first refer back to the Jablonski diagram of Figure 9.1 where we depicted the T_1 level to be lower in energy than the S_1 level. Since delayed fluorescence as we discussed it in the text is a result of the molecule transferring from the triplet manifold back to S_1 , the molecule in the triplet state must obtain additional energy to achieve this transfer. This can easily be achieved through thermal activation of the T_1 state, i.e.,



Thus, one would expect that an increase in temperature would increase this thermal activation and therefore increase the amount of delayed fluorescence.

8. We can use the Stern-Volmer relationship (Equation 9.20) calculate the approximate concentration of Q necessary for 50% quenching. Since

$$\frac{\phi_f^0}{\phi_f} = 2$$

for 50% quenching, the Stern-Volmer relationship reduces to

$$[Q]_{50\%} = \frac{1}{(k_{dc} \tau_0)}$$

We have previously noted that $k_{dc} \approx 10^{10}$ and given that $\tau_0 \approx 10^{-9}$ second for a good fluorescer, we have

$$[Q]_{50\%} = \frac{1}{10^{10} \times 10^{-9}} = \frac{1}{10} = 0.1 \text{ M.}$$

Even if τ_0 were 10 fold greater, we still need concentrations in the range of 0.01 M to achieve 50% quenching. Thus, relatively large concentrations of quenchers are necessary to achieve effective quenching. This derivation also implies that it is possible to minimize the effects of dynamic quenching by diluting the solution such that the quencher concentration is far below the calculated 0.1 M.

9. The predicted effect of each parameter on ϕ_f are as follows:

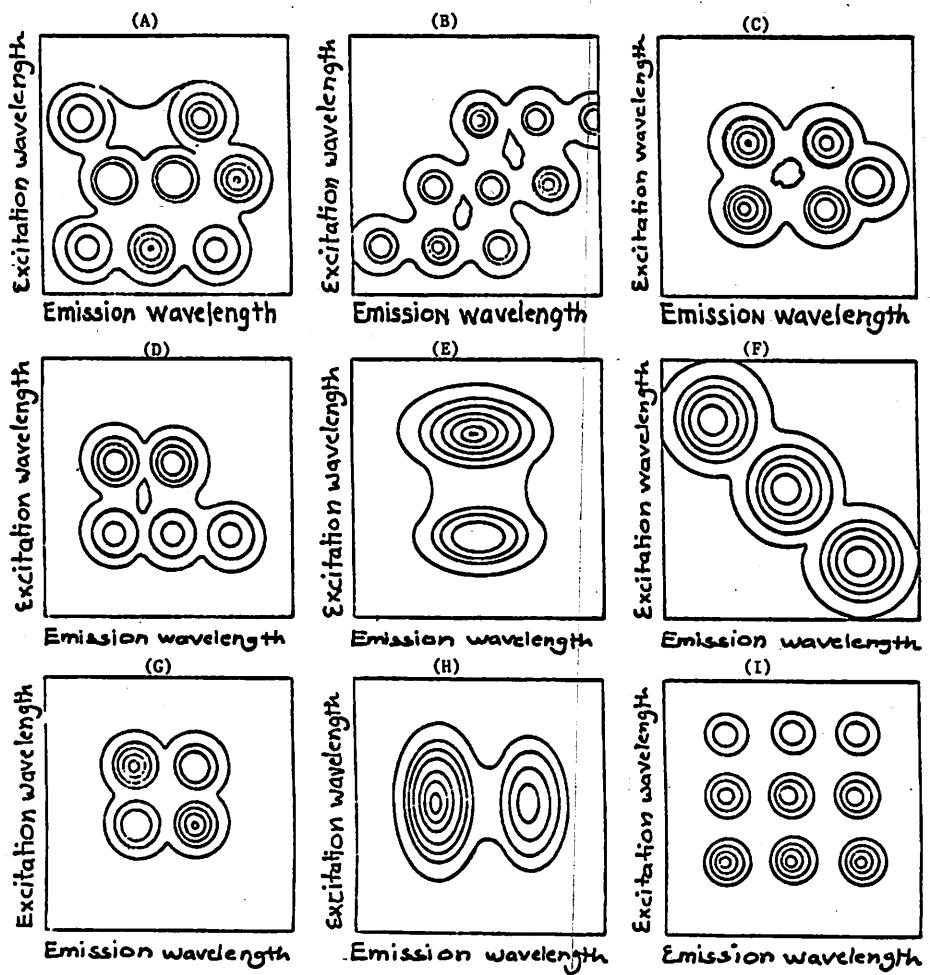
- a) lowering the temperature - a lowering of the temperature of the solution should decrease the number of collisions which lead to non-radiative deactivation. Thus, the quantum yield should increase as the temperature is lowered.
- b) raising the temperature - raising the temperature of the solution should have the opposite effect of lowering the temperature of the solution. Since the number of deactivating collisions will increase with temperature, the quantum yield should decrease.
- c) changing the concentration of the fluorophore - a small change in concentration should not affect the quantum yield. However, large increases in the concentration of some fluorophores may produce excited dimers which will affect the quantum yield. In addition, there is usually an overlap between the fluorescence spectrum and the first excited absorption spectrum such that the relative fluorescence intensity decreases with increasing concentration of the fluorophore at high concentrations of fluorophore.
- d) and e) adding a static or dynamic quencher - the addition of a static quencher should decrease the quantum yield as discussed in Problem 6.
- f) the solvent viscosity - the quantum yield of fluorescence tends to increase with increased solvent viscosity since the number of deactivating collisions decreases.

10. If we assume that the excitation spectrum is independent of the monitored emission wavelength and that the emission spectrum is independent of the excitation wavelength, then for a pure component the emission spectral profile should not change as the excitation wavelength is varied. In addition, the excitation profile should not change as the monitored emission wavelength is varied. Thus, if the emission and excitation spectral profiles change, more than one component is indicated. Moreover, the number of times each profile changes is the minimum number of components contributing to each contour map.

(A) - three components, (B) three components, (C) two components, (D) two components, (E) one component, (F) three components, (G) two components, (H) one component and (I) one component.

One cannot say with certainty how many components are present for two major reasons. First, there may be additional components which are linear combinations of other components and this would not be apparent in a contour map. Secondly, there may be a component whose intensity information is lost in the noise of the major components.

11. In absorption spectroscopy, one measures the difference between the logarithm of the incident beam, I_0 , and the logarithm of the transmitted beam, I_T . Both beams are very intense and Beer's law requires that the difference between I_T and I_0 be very small. Thus, this is a very difficult measuring process and as indicated in the text with Equation 9.19, detection limits for a good



Figure, Problem 10

absorber are in the range of 1×10^{-8} M. In fluorescence spectroscopy, the fluorescence signal is typically measured above a constant background contributed by the detector and the electronics. This is a much easier measuring process and consequently a good fluorescer that is also a good absorber can easily be measured in the range of 1×10^{-12} M.

12. We have previously related the intensity of fluorescence and the absorbance using Equation 9.18 in the text. We should insert another constant into this equation to compensate for instrumental factors such as collection geometry and detector sensitivity. Thus, Equation 9.18 becomes

$$I_f = 2.303 k \phi_f I_0 \epsilon bc ,$$

where k is a constant which corrects for instrumental factors.

Now if we assume that the two molecules in our problem are excited at the same wavelength, I_0 and the the fluorescence is measured in the same size cell, then our equation reduces to

$$I_f = K' \phi_f \epsilon c$$

where all of the constants are now incorporated into a new constant, K' . Thus, a plot of intensity of fluorescence, I_f , versus concentration, c, gives a slope of $K' \phi_f \epsilon$. Consequently, the slope for the first molecule is given by

$$K' (0.01)(10^5) = 10^3 K' .$$

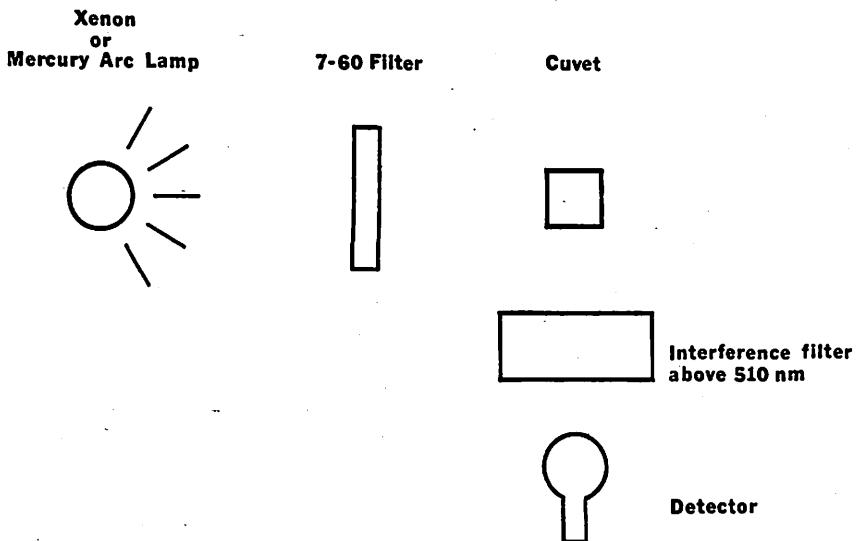
For the second molecule, we have

$$K' (0.10)(10^3) = 10^2 K' .$$

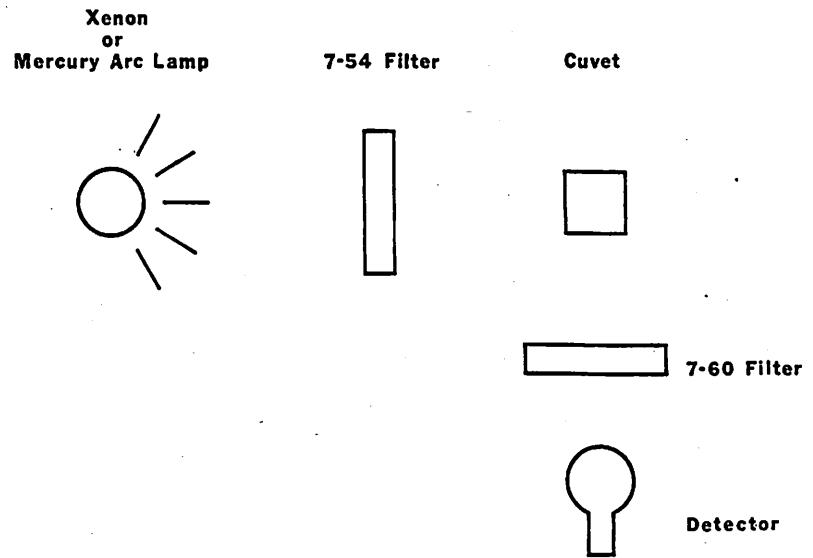
Therefore, the first molecule will give a calibration curve slope which is ten times that of the second.

13. Using Figures 9.2, 9.5 and 9.9, we can select optimum wavelengths for the design of our filter fluorometer. We note from Figure 9.2 that perylene absorbs over the range of 325nm to 475nm and emits over the range of ~410nm to 525nm. In contrast, anthracene absorbs over the range of ~300nm to ~387nm and emits over the range of ~360nm to ~500nm. Accordingly, our two filter fluorometers can be designed to incorporate these wavelength differences. Note that both systems are designed for an optimum excitation wavelength and an optimum emission wavelength for each component.
14. A quick inspection of the data shows that the first two points are non-linear in fluorescence intensity versus concentration. Moreover, the latter four points cover the concentration range of the diluted sample. Therefore, our calibration curve is plotted from "0" to "1.0" ppm. Our sample had an emission intensity of 8.44 units which correspond to 0.7 ppm. However, this sample was diluted 100-fold before reading. Consequently, the original

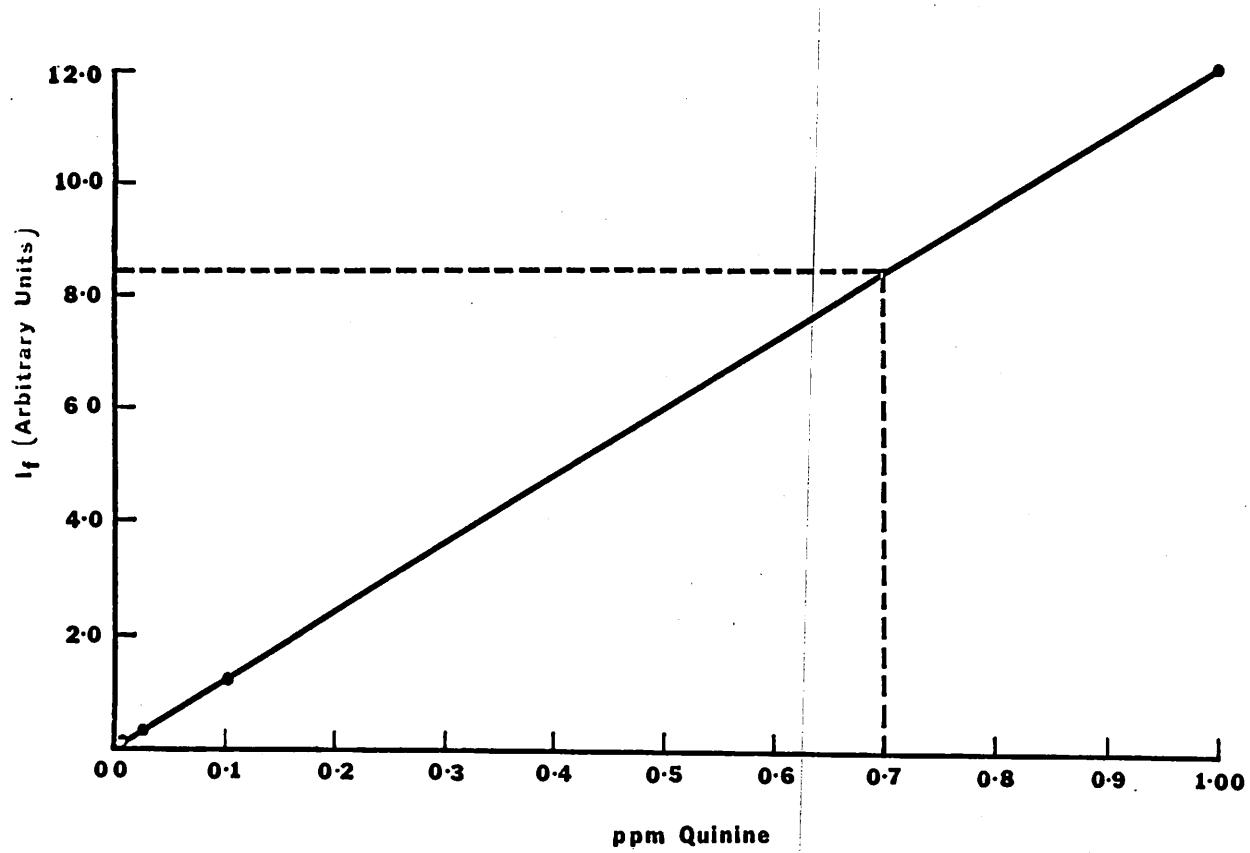
Design 1 (Perylene in presence of Anthracene)



Design 2 (Anthracene in presence of Perylene)



Figures, Problem 13



Figure, Problem 14

concentration of the sample is 70 ppm quinine.

15. Recall in problem #12 that we indicated that the intensity of fluorescence is given by

$$I_f = 2.303 k \phi_f I_0 \text{ sbc}$$

where k is a compensating constant for instrumental factors.

a) It is useful to derive a table of the pertinent information for each set of conditions.

<u>λ_{ex}</u>	<u>λ_{em}</u>	<u>ϵ</u>	<u>ϕ_f</u>	<u>Relative Lamp Output</u>	<u>Relative S-5 Response</u>
250nm	500nm	15,000	Same as 500nm	0.5	30
500nm	600nm	4,000	Same as 250nm	1.3	3

Therefore, the ratio of the signal with 250nm excitation to that with 500nm excitation is given by

$$\frac{I_f(250\text{nm})}{I_f(500\text{nm})} = \frac{k_{250} I_0(250) \epsilon_{250}}{k_{500} I_0(500) \epsilon_{500}} = \frac{0.5 \times 30 \times 15,000}{1.3 \times 3 \times 4,000} = \frac{225,000}{15,600} = 14.42 .$$

Consequently, the measured intensity of fluorescence should be ~ 14 times more intense with excitation at 250nm than for excitation at 500nm.

b) Some of the assumptions are 1) that the same sample cuvette is used, 2) the collection efficiency, grating efficiency, etc. are

the same at each wavelength and 3) that absorption at 250nm is low such that Equation 9.18 is applicable.

16. One would predict that optimum energy transfer would occur when the energy of the "donor" triplet is slightly greater than that of the "acceptor" triplet. If the energy level of the "donor" were "lower" than the "acceptor", population of the "acceptor" triplet would not occur.

CHAPTER 10

1. The range of wavelengths from a continuum source passed by the slit are much broader than the absorption line profile, resulting in unabsorbed light (wavelengths) falling on the detector at all times. A sharp line source profile is narrower than the absorption line profile, and so the total width of radiation is absorbed, following Beer's law.

2. $N_i/N_0 = g_i/g_0 (e^{-(E_i-E_0)/kT})$

For example, for Cs at 3000°K:

$$E = h\nu ; h = 6.626 \times 10^{-27} \text{ erg-sec}$$

$$k = 1.3805 \times 10^{-16} \text{ ergs/K}$$

$$\nu = c/\lambda ; c = 2.998 \times 10^{10} \text{ cm/sec}$$

$$\text{For } 8521 \text{ \AA} = 8.521 \times 10^3 \times 10^{-8} \text{ cm} = 8.521 \times 10^{-5} \text{ cm} \quad (1 \text{ \AA} = 10^{-8} \text{ cm})$$

$$\nu = 2.998 \times 10^{10} \text{ cm sec}^{-1} / 8.521 \times 10^{-5} \text{ cm} = 3.518 \times 10^{14} \text{ sec}^{-1}$$

$$N_i/N_0 = 2e^{-h\nu/kT} =$$

$$2e^{-(6.626 \times 10^{-27} \text{ erg-sec} \times 3.518 \times 10^{14} \text{ sec}^{-1}) / (1.3805 \times 10^{-16} \text{ erg K}^{-1} \times 3 \times 10^3 \text{ K})}$$

$$= 2e^{-5.628} = 2(3.594 \times 10^{-3}) = 7.19 \times 10^{-3}$$

$$\text{Similarly, for Na at } 5890 \text{ \AA}, 2000 \text{ K}, N_i/N_0 = 9.7 \times 10^{-6}$$

These numbers are slightly smaller than those in the table, taken from Walsh, Spectrochim. Acta, 7, 108 (1955).

3. AAS: Just need to resolve the resonance line from other source lines.

AES: Need to resolve from flame background. Therefore, more critical (higher resolution needed).

4. To dissociate refractory forming compounds.

5. To suppress ionization and hence, minimize interference from ionizable elements.

6. To eliminate detection of d.c. signals from the flame.

7. Spectral (line or molecular band overlap), chemical (refractory compound formation), ionization (free electrons added in the flame), physical (properties of the solution).

8. To increase sensitivity or response due to improved aspiration/atomization properties.

9. $\%T_{12} = 100 - 30\% \text{ absorption} = 70\%$

Sensitivity = ppm at 1% absorption = 99% $T = T_s$

$-\log T = kC$

$(-\log T_{12})/(-\log T_s) = kC_{12}/kC_s;$

$(-\log 0.70)/(-\log 0.99) = 12 \text{ ppm/s ppm}$

$0.155/0.0044 = 12 \text{ ppm/s ppm}; s = 0.341 \text{ ppm} = \text{sensitivity}$

10. Plot 0, 0.5, 1.0 $\mu\text{moles Li}$ added vs. 23.0, 45.3, 68.0 signal.

Extrapolate $\rightarrow 0.51 \mu\text{moles Li}$ in sample (0.500 mL) = 1.02 $\mu\text{moles/mL}$

$1.02 \mu\text{moles/mL} \times 6.94 \mu\text{g}/\mu\text{mole} = 7.1 \text{ ppm}$

(or mathematical proportionality provides same answer)

11. a) From calibration curve, test sample is 15.5 ppm Ba

$15.5 \mu\text{g/mL} \times 100 \text{ mL} \times (100/20) = 7,750 \mu\text{g}/100 \text{ mL}$

$= 7.75 \text{ mg Ba}/21.0 \text{ mg Ba compound} = 36.9\% \text{ Ba in compound}$

b) $\text{C}_9\text{H}_{16}\text{N}_4\text{O}_7 + \text{Ba}^{2+} \rightarrow (\text{C}_9\text{H}_{14}\text{N}_4\text{O}_7)\text{Ba} + 2\text{H}^+$
(At.wt. 137.3) (M.W.=427.6)

Theoretical % Ba in compound = $137.3/427.6 \times 100 = 32.1\%$

\therefore percent purity = $(36.9/32.1) \times 100 = 115.0\%$

c) For low absorbance readings, the "noise" is about equal to the typical standard deviation of the absorbance signal:

$$N = (7 + 3 + 4)/3 = 4.7$$

For the 1- and 4-ppm solutions, the average signal is

$$S = 1/2([44/1\text{ppm}] + [178/4 \text{ ppm}]) = 44.2 \text{ ppm}$$

Therefore, $S/N = 44.2/4.7 = 9.5 \text{ ppm}^{-1}$

For $S/N = 2$, and a linear calibration curve,

$$C_{D.L.} = 2/9.5 \text{ ppm} = 0.2 \text{ ppm}$$

12. The enhancing effect of the potassium is due to suppression of Na ionization in the flame as K ionization adds electrons to the flame. The result is a greater population of Na atoms available for thermal excitation.

13. See text

14. See text

15. See text

16. See text

17. In atomic fluorescence, lines are emitted and can be readily isolated. In atomic absorption, very high resolution is needed to isolate the absorption line profile (see also Problem 1).

18. No. Each has advantages in certain wavelength regions. See text discussions.

19. a) Using $g = 2J + 1$, and the definition of the term symbol for the spectroscopic state as M_{L_J} , the value of J for the Ca 422.673-nm line is seen to be 0 for the ground state and 1 for the upper state. Therefore,

$$g_u/g_0 = [2(1) + 1]/[2(0) + 1] = 3/1 = 3$$

In a similar manner, the ratios of g_u/g_0 for either the sodium or the potassium doublet are calculated to be 4/2 and 2/2 for the shorter- and longer-wavelength transitions, respectively.

b) For Ca at 422.673 nm, and an entrained air/argon-hydrogen flame ($^{\circ}\text{K} = 1577^{\circ}\text{C} + 273^{\circ} = 1850 \text{ K}$),

$$\begin{aligned} \nu &= c/\lambda = (2.9979 \times 10^{10} \text{ cm/sec})/(422.673 \text{ nm} \times 10^{-7} \text{ cm/nm}) \\ &= 7.0927 \times 10^{14} \text{ sec}^{-1} \end{aligned}$$

$$\begin{aligned} E_u - E_0 &= h\nu = (6.6262 \times 10^{-27} \text{ erg-sec})(7.0927 \times 10^{14} \text{ sec}^{-1}) \\ &= 4.6998 \times 10^{-12} \text{ erg} \end{aligned}$$

$$N_u/N_0 = g_u/g_0 \exp [-(E_u - E_0)/kT]$$

$$= 3 \exp [-4.6998 \times 10^{-12} \text{ erg} / (1.3806 \times 10^{-16} \text{ erg-K}^{-1})(1850 \text{ K})]$$

$$= 3.06 \times 10^{-8}$$

In a similar manner, the ratio is calculated to be 4.14×10^{-6} and 7.89×10^{-5} in air-acetylene and nitrous oxide-acetylene, respectively.

In an entirely analogous manner, the ratios for the three flames for the Na 588.9963-nm line ($g_u/g_0 = 2$) are calculated to be 3.68×10^{-6} , 1.25×10^{-4} , and 1.03×10^{-3} ; for the Na 589.5930 line ($g_u/g_0 = 1$), they are 1.87×10^{-6} , 6.30×10^{-5} , and 5.21×10^{-4} , respectively. The corresponding set of ratios for the K 764.494-nm line are 7.63×10^{-5} , 1.15×10^{-3} , and 5.87×10^{-3} ; for the K 769.901-nm line, they are 4.10×10^{-5} , 6.07×10^{-4} , and 3.06×10^{-3} .

c) The easiest approach is simply to ratio the N_u/N_0 ratios for the pairs of lines in question (at each flame temperature). Starting with the Maxwell-Boltzmann equation, and letting 1 be the lower-wavelength and 2 be the higher-wavelength line of the doublet, we have

$$\frac{N_1}{N_2} = \frac{g_1}{g_2} \exp [-(E_1 - E_2)/kT]$$

$$= \frac{g_1}{g_2} \exp [(1/\lambda_2 - 1/\lambda_1)hc/kT]$$

For the sodium doublet at 1850 K,

$$\frac{N_{588.9963 \text{ nm}}}{N_{589.5930 \text{ nm}}} = \frac{2}{1} \exp [\frac{1}{589.5930} - \frac{1}{588.9963}] \left(\frac{1}{10^{-7}} \right) \left(\frac{2.9979 \times 10^{10}}{1.3006 \times 10^{-16}} \right) \left(\frac{6.6262 \times 10^{-27}}{1850} \right)$$

$$= 1.974$$

Values of 1.980 and 1.985 are obtained for 2523 and 3228 K. A similar approach for the K doublet gives ratios of 1.862, 1.898, and 1.920 for the three flames.

20. For A, $S \approx 24$, $N_{pp} \approx 17$

$$S/N_{rms} \approx 24(5)/17 = 7$$

D.L. ($S/N = 2$) = $2/7 = 0.28 \approx 0.3$ of the concentration giving rise

to the plot shown. For B, $S/N_{rms} \approx 100$; D.L. ($S/N = 2$) ≈ 0.02 .

CHAPTER 11

1. Atomic absorption requires a separate radiation source for each element, which complicates the optical arrangement as well as electronics.
2. (a) The compounds of the ions are thermally dissociated to the free atoms. Hence, there is transfer of electrons within the compound. There may also be electrons present from the thermal ionization of other atoms. (b) The color observed results from the fact that the emission lines of the atoms occur in the visible region. (c) Colors of main emission lines: Li, 671 nm, red (+ yellow line); Na, 589 nm, yellow; K, 766 nm, red (+ violet line → lavender - red); Rb, 780 nm, red; Cs, 455 nm, blue (+ red line); Be, 235 nm, u.v.; Mg, 285 nm, u.v.; Ca, 423 nm, violet (+ red and yellow lines → orange red); Sr, 471 nm, blue (+ red and yellow lines); Ba, 553 nm green (+ red, yellow and blue lines).
3. These elements emit in the vacuum u.v. region, where air absorbs radiation, and is unaccessible by ordinary instruments. Emission from gases could be determined by placing them in an evacuated quartz container containing electrodes, and passing an arc through them, as in a glass discharge or hollow cathode lamp. A vacuum u.v. instrument would be required for measurement.
4. The source would be relatively noisy, and there would be a high degree of ion formation.
5. This technique may give reasonable resolution, depending on extent of spark wander and the dimension. Vaporization/excitation by means of a laser source may provide improved resolution.
6. Mg, Zn, Cu, Th, Zr, Mn, Ca, Si, Al, (a Mg alloy)
7. Peak heights (cm): Sample 6.0, Sample +0.005 $\mu\text{g/mL}$ 14.0; sample +0.01 $\mu\text{g/mL}$ 21.0; Sample +0.02 $\mu\text{g/mL}$ 41.0. A standard additions plot reveals a sample concentration of 0.0035 $\mu\text{g/mL}$ Mn. Since the sample was diluted 10-fold, the original concentration is 0.035 $\mu\text{g/mL}$.
8. Peak heights (mm): 31.5, 35.3, 31.2, 29.9, 29.8, 32.9, 29.5; Mean = 31.4; $\sum(\bar{x}-x_i)^2 = 25.93$; $\sigma = [\sum(\bar{x}-x_i)^2/(N-1)]^{1/2} = (25.93/6)^{1/2} = \pm 2.08 \text{ mm}$
The mean signal (31.4) corresponds to 0.035 $\mu\text{g/mL}$ Mn. Hence, $\pm 2.1 \text{ cm}$ corresponds to $\pm 0.0023 \mu\text{g/mL}$. r.s.d. = $(2.08/31.4) \times 100\% = \pm 6.6\%$
9. (a) The internal standard should be chemically similar to the analyte, with spectral lines nearby. (b) A spectrochemical buffer should consist of a salt with a readily ionizable cation, e.g., Li_2CO_3 . (c) A matrix diluent should have volatility properties similar to the analyte elements, e.g.,

readily volatilized with trace elements.

10. From the Saha equation, the fraction ionized at 2500K is 1.24×10^{-9} ; at 5000K it is 1.11×10^{-3} . Hence, ionization is not appreciable, and most of the atoms remain as atoms. See Example 10.1 for calculation of the relative fraction of ground state atoms available for absorption at the two temperatures. From Table 10.1, most reside in the ground state, and so the sensitivity (ignoring compound formation) should remain constant.

11. 0.13% Si, 1.4% Na

CHAPTER 12

1. a) $6.73 \text{ ppm} \times 90 \text{ Hz/ppm} = 605.7 \text{ Hz}$

$605.7 \text{ Hz} - 528.4 \text{ Hz} = 77.3 \text{ Hz}$

$77.3 \text{ Hz}/90 \text{ Hz/ppm} = 0.859 \text{ ppm from TMS}$

b) $6.73 \text{ ppm} \times 200 \text{ Hz/ppm} = 1346.0 \text{ Hz}$

$0.859 \text{ ppm} \times 200 \text{ Hz/ppm} = \underline{171.8}$

1174.2 Hz

2. a) ethyl alcohol

b) p-(t-butyl)toluene

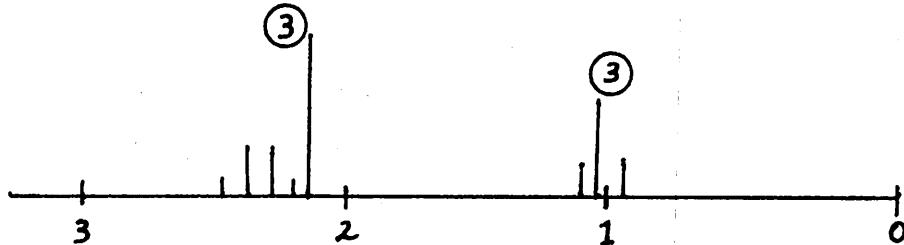
c) 1,2-dibromo-2-methylpropane

d) 1,1,2-tribromoethane

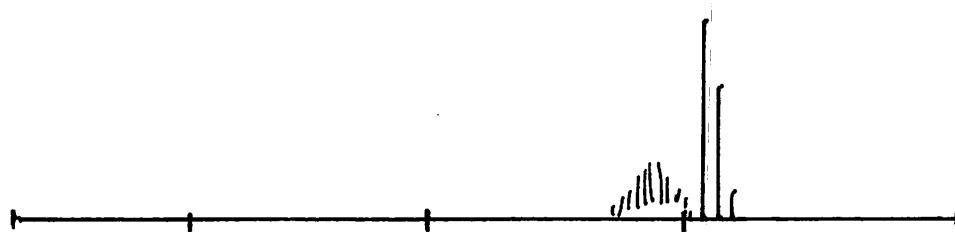
e) 1,1-dibromoethane

f) ethyl bromide

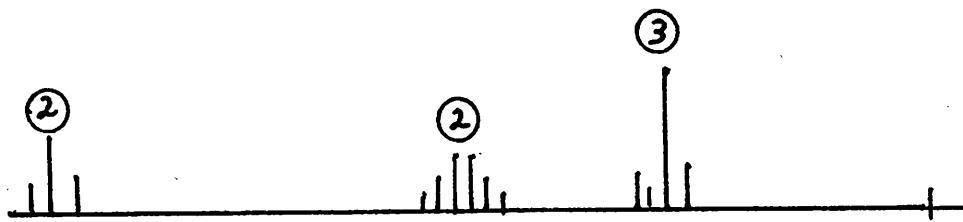
3.



4.



Propane: triplet, 0.99 ppm (area 6); multiplet, 1.29 ppm (area 2)



1-Nitropropane: triplet, 1.01 ppm (area 3); multiplet 2.00 ppm (area 2); triplet 4.31 ppm (area 2)

5. a) $90 \times 10^6 \text{ Hz}/21,138 \text{ gauss} = 4258 \text{ Hz/gauss}$

b) $4,258 \text{ Hz/gauss} \times 23,487 \text{ gauss} = 100 \text{ MHz}$

c) $\gamma_c = 25.1 \text{ MHz}/23,487 \text{ gauss} = 1,068.7 \text{ Hz/gauss}$

$80 \text{ MHz}/4,258 \text{ Hz/gauss} = 18,788 \text{ gauss}$

$1,068.7 \text{ Hz/gauss} \times 18,788 \text{ gauss} = 20 \text{ MHz}$

6. a) A frequency sweep spectrometer is one in which the strength of the magnetic field is held constant and the spectrum is obtained by varying the RF frequency.

b) Spin lattice relaxation is the process by which nuclear spins which are not in equilibrium along the direction of the main magnetic field transfer energy to their surroundings and attain equilibrium. This process occurs when the sample is first placed in the magnet and following any perturbation such as sweeping through the signal or applying an RF pulse. This is an exponential rate process characterized by the spin lattice relaxation time constant T_1 .

c) Chemical shift can be defined in three ways: Described as a phenomenon, chemical shift refers to the observation that nuclei in different environments have (slightly) different resonance frequencies. Described as an effect or action, chemical shift refers to the change in resonance frequency of some known compound by the introduction of some structural group, e.g., the chemical shift effect of a nitro group on the ^1H benzene signal. Finally, chemical shift can be defined very specifically as the location of a signal relative to the standard reference compound TMS, as given by Eqn. 12.7 or Eqn. 12.8.

d) TMS is the universal standard reference compound, tetramethylsilane $(\text{CH}_3)_4\text{Si}$.

e) Ring current is the extra circulation of electrons around aromatic rings when they are placed in a magnetic field. This "current" causes an additional magnetic field in the vicinity of aromatic rings which produces spacially related changes in chemical shifts.

f) Lanthanide Induced Shift. The differential displacement of signals in the presence of various paramagnetic lanthanide complexes.

g) Pulse FT NMR is the most recent technique in which all the signals from a given kind of nuclide are excited simultaneously by a strong, brief R.F. pulse. The resulting signals from all the different environments give a complex interferogram which is digitized in a few seconds or less and stored in a computer. The corresponding spectrum (frequencies) Transformation of the interferogram. Pulse FT spectrometers offer much greater effective sensitivity, permitting examination of less abundant nuclides such as ^{13}C , ^{18}N , ^{17}O , and so forth.

h) Nuclear Overhauser Enhancement, or the Nuclear Overhauser Effect, is the increase of signal intensity from one kind of nuclide, e.g., ^{13}C , when another such as ^1H is decoupled from it.

i) A special experiment in which the proton decoupler is positioned slightly away from the proton spectrum while measuring a ^{13}C spectrum. This permits the one-bond C-H coupling to reappear (attenuated) in the carbon spectrum. In this case, CH_3 carbons appear as quartets, CH_2 's as triplets, and CH 's as doublets.

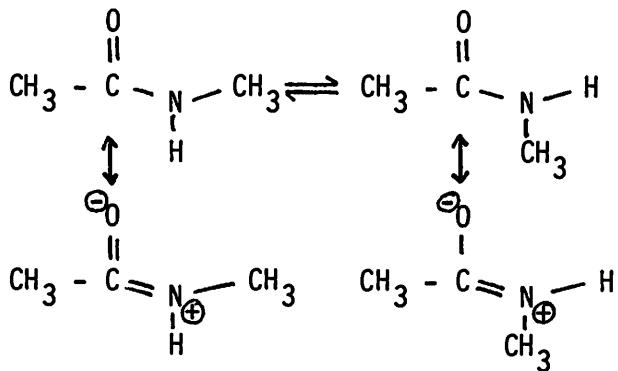
7. a) $320 \text{ Hz}/(90 \text{ Hz}/\text{ppm}) = 3.55 \text{ ppm}$

b) $400 - 180 = 220 \text{ Hz}$

$220 \text{ Hz}/(60 \text{ Hz}/\text{ppm}) = 3.67 \text{ ppm}$

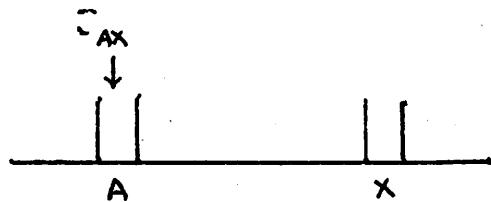
c) $7.3 \text{ ppm} \times (400 \text{ Hz}/\text{ppm}) = 2920 \text{ Hz}$

8.

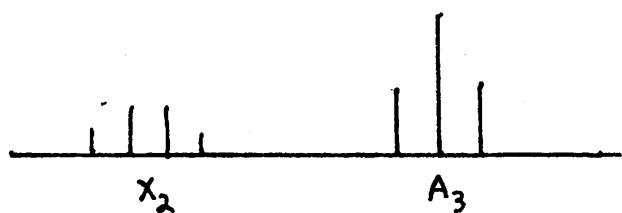


The strong resonance interaction between the nitrogen electrons and the carbonyl group produces a barrier to rotation. The two rotamers exchange sufficiently slowly that the two structurally different N-CH_3 groups give different signals in the NMR.

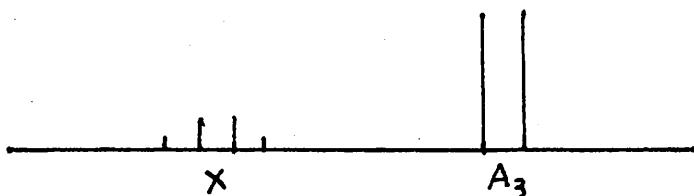
9. a)



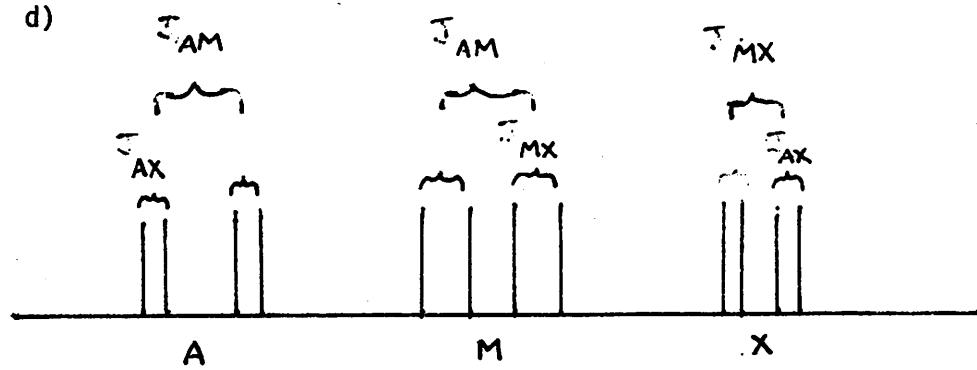
b)



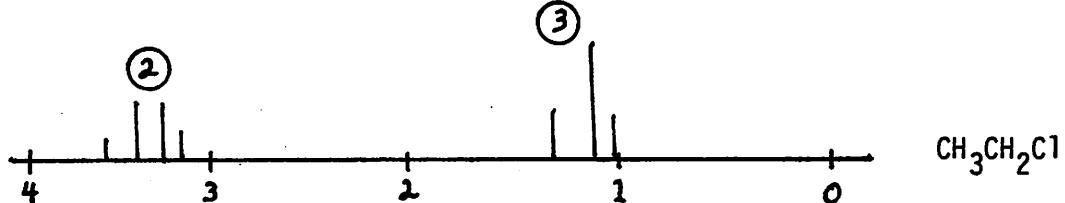
c)



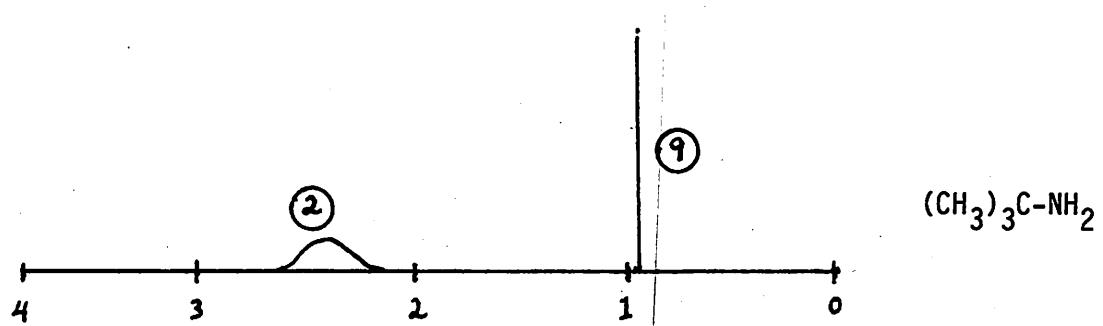
d)



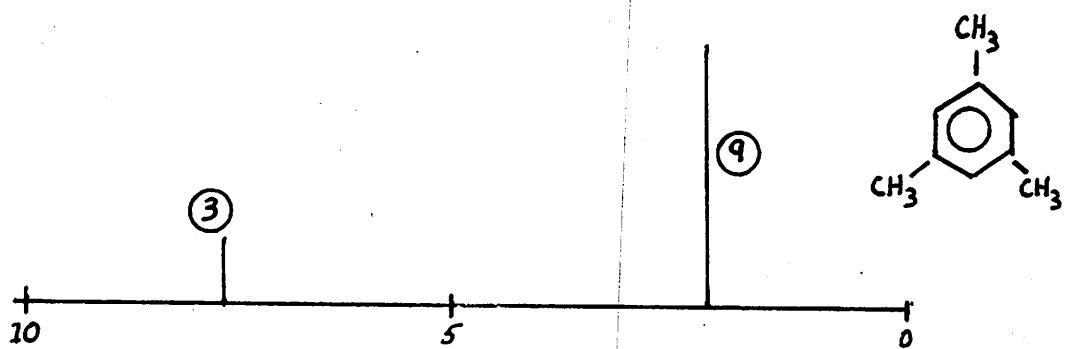
10. a)



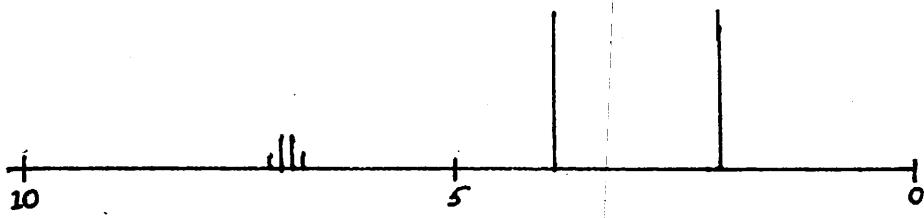
b)



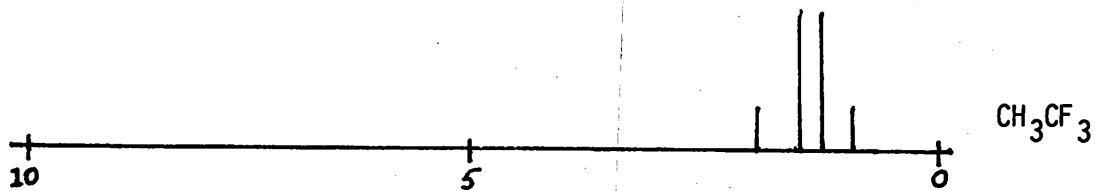
c)



d)



e)



11. 1) 2.2 ppm signal is from three H's of the CH_3 group in toluene.
∴ integral value is 5 units per H.

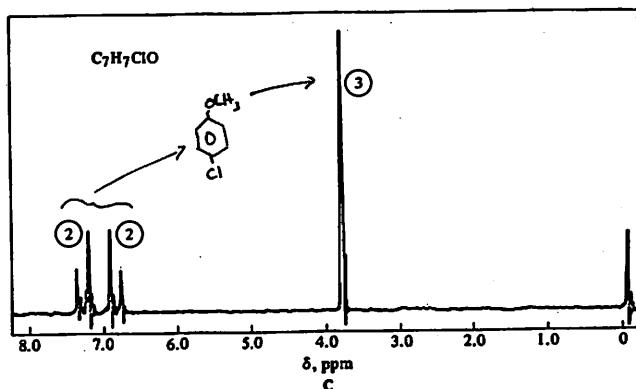
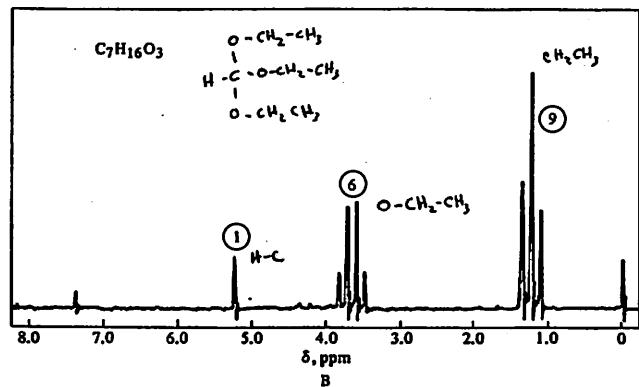
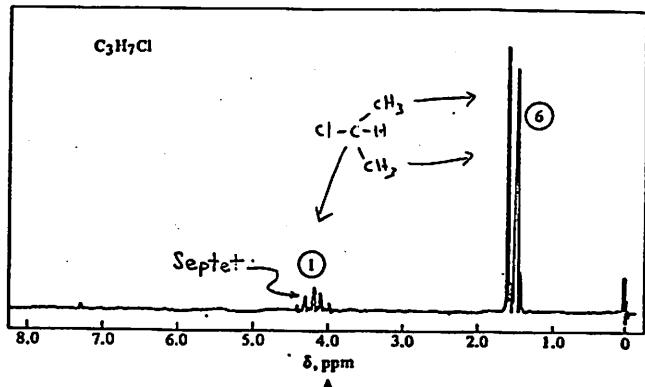
2) The 5 H's of the toluene ring will contribute $5 \times 5 = 25$ integral units to the signal at 7.3 ppm.

∴ $85 - 25 = 60$ integral units of the signal at 7.3 ppm arise from benzene.

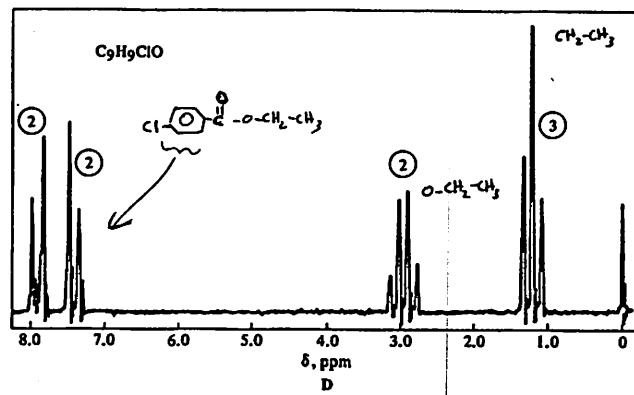
3) If there was one benzene for each toluene, that benzene would be expected to give 5×6 H's = 30 integral units.

∴ $60 \text{ integral units} / 30 \text{ integral units per benzene} = 2$
benzene:toluene ratio 2:1

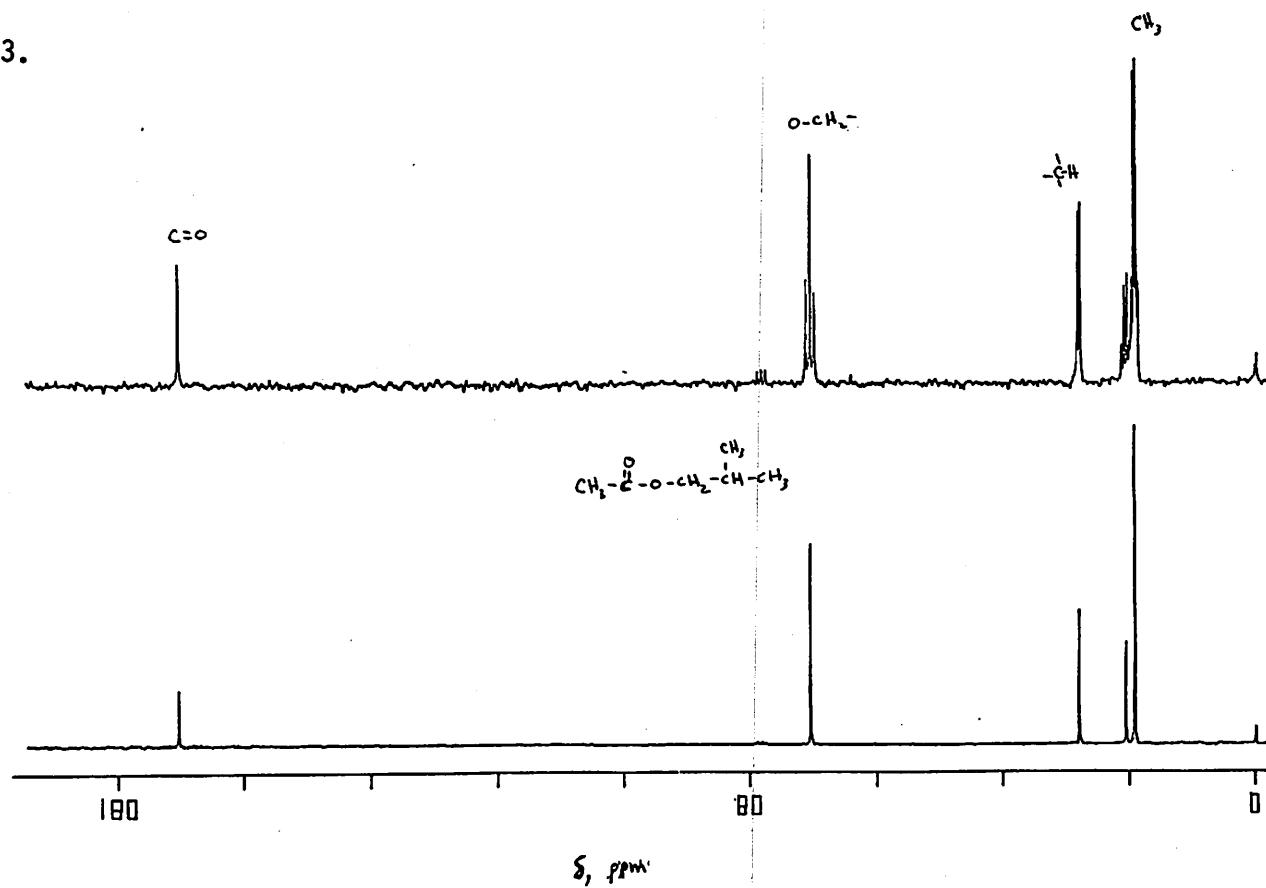
12. See notes and structures on spectra.



Spectra for Problem 12

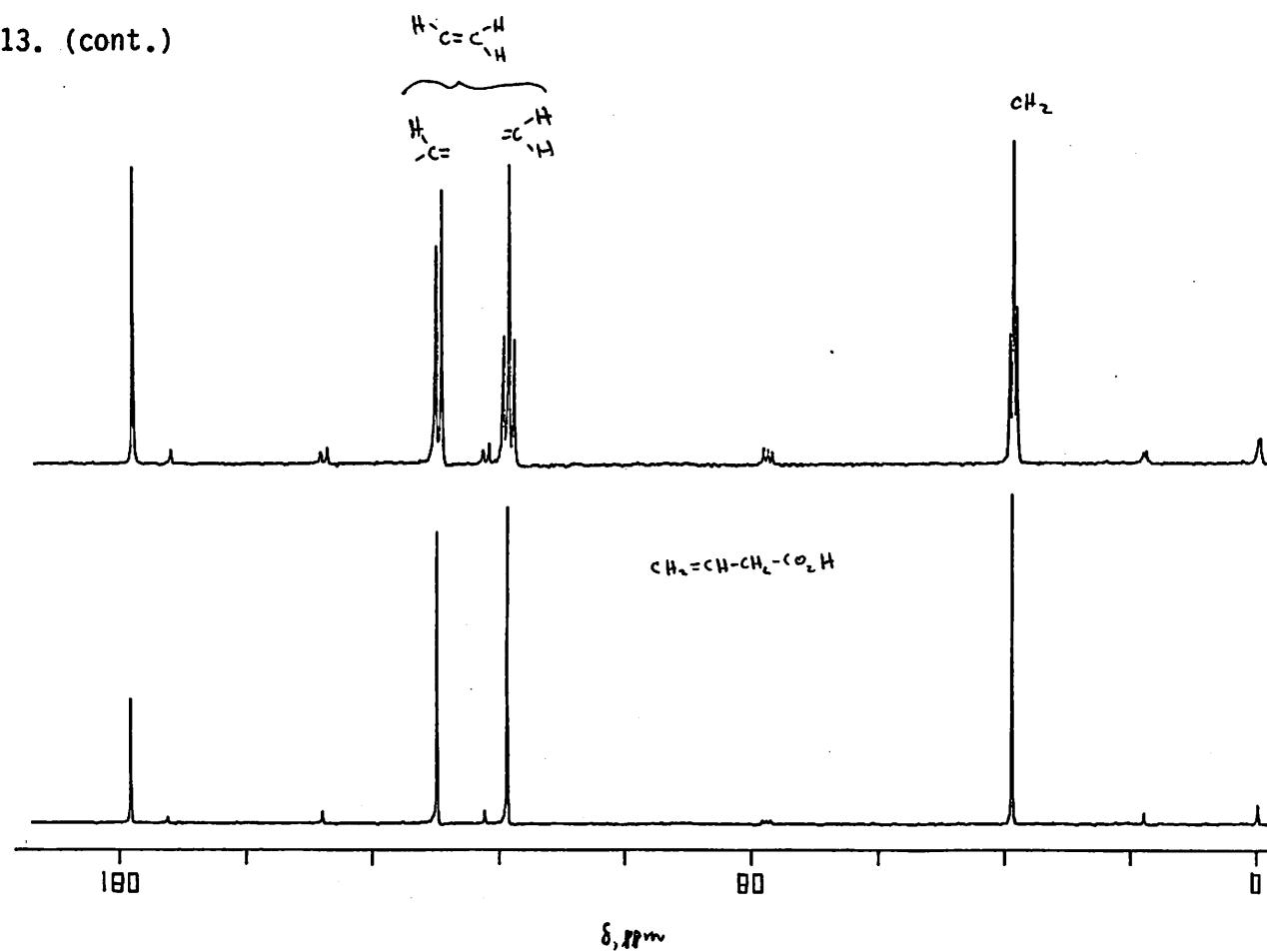


13.



12-88

13. (cont.)



14. A = HCFC1 - CFC1₂

B = HCC1₂ - CF₂C1

CHAPTER 13

1. $h\nu = g\beta H$, therefore $H = h\nu/g\beta$

e.g., $H = \frac{6.6262 \times 10^{-27} \text{ erg-sec} \times 9.40 \times 10^9 \text{ sec}^{-1}}{0.9273 \times 10^{-20} \text{ erg/gauss} \times 2.800} = 2399 \text{ gauss}$

2399, 5869 and 8931 gauss for $g = 2.800$

3420, 8367 and 12733 gauss for $g = 1.964$

2. $H_1 = h\nu/g_1\beta$, $H_2 = h\nu/g_2\beta \therefore H_1 - H_2 = \frac{h\nu}{\beta} (1/g_1 - 1/g_2)$, where $g_1 < g_2$

e.g., $H_1 - H_2 = \left(\frac{6.6262 \times 10^{-27} \text{ erg-sec} \times 9.40 \times 10^9 \text{ sec}^{-1}}{0.9274 \times 10^{-20} \text{ erg/gauss}} \right) \times \left(\frac{1}{2.045} - \frac{1}{2.160} \right)$

= 174.9 gauss

$\Delta H = 174.9, 427.8$ and 651.1 gauss for $g_1 = 2.045, g_2 = 2.160$

$\Delta H = 243.6, 596.0$ and 907.0 gauss for $g_1 = 1.960, g_2 = 2.110$

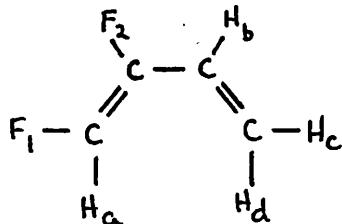
3. $E = h\nu = 33.3586 \times 10^{-12} \text{ cm}^{-1} \text{ sec} \times 9.400 \times 10^9 \text{ sec}^{-1} = 0.314 \text{ cm}^{-1}$

0.314, 0.767 and $1.168 \text{ cm}^{-1}/\text{molecule}$

4. Eqn. 13.9, $h = 6.6262 \times 10^{-27} \text{ erg-sec}$

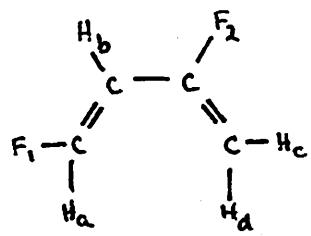
<u>T (°K)</u>	<u>9.4 GHz</u>	<u>23 GHz</u>	<u>35 GHz</u>
4	0.8933	0.7588	0.6571
20	0.9777	0.9463	0.9194
77	0.9942	0.9858	0.9784
298	0.9985	0.9963	0.9944

5. Eqn. 13.12

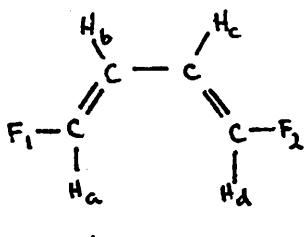


No H's or F's equivalent, hence

$(2 \times 1 \times \frac{1}{2} + 1)^6 = 64$ lines

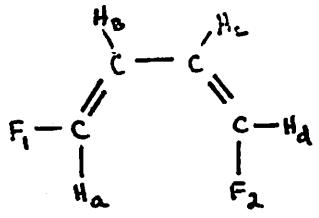


No H's or F's equivalent, hence 64 lines



F_1 and F_2 , H_a and H_d , and H_b and H_c are equivalent, hence

$$(2 \times 2 \times \frac{1}{2} + 1)^3 = 27 \text{ lines}$$



No H's or F's equivalent, hence 64 lines

6. Eqn. 13.11:

There is no difference in the number of lines expected for the anion and cation, providing there is not distortion of symmetry lower than O_n . The only change expected is that the hyperfine coupling constants will be slightly larger for the radical cation.

$$(2 \times 1 \times 3/2 + 1) (2 \times 6 \times \frac{1}{2} + 1) = (4) (7) = 28 \text{ lines}$$

7. Eqn. 13.11:

$$(2 \times 1 \times 3/2 + 1) (2 \times 2 \times \frac{1}{2} + 1) (2 \times 4 \times \frac{1}{2} + 1) = 60 \text{ lines for copper compound}$$

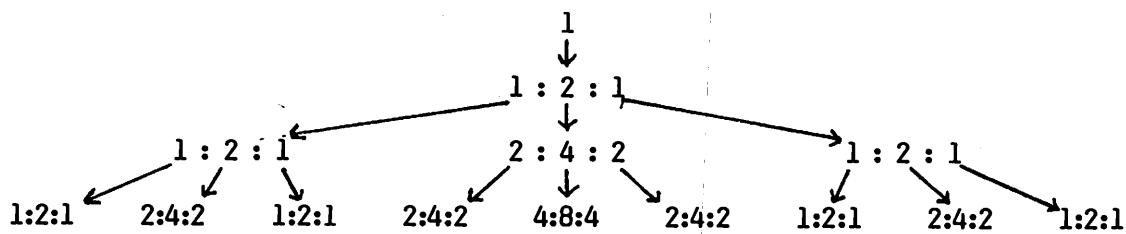
$$(2 \times 1 \times 7/2 + 1) (2 \times 2 \times \frac{1}{2} + 1) (2 \times 4 \times \frac{1}{2} + 1) = 120 \text{ lines for vanadium compound}$$

$$8. (2 \times 4 \times \frac{1}{2} + 1) = 5$$

Tetrahedral P_4^- would have 4 equivalent phosphorus atoms ($I = \frac{1}{2}$). For a binomial distribution (Table 13.2), the five peaks would have intensity ratios of 1:4:6:4:1.

9. From Question 5, the trans, trans-compound is seen to have two different pairs of chemically equivalent H's, and one pair of chemically equivalent F's to cause spectral splitting. The assumption that none of the lines overlap is essentially equivalent to saying that the three hyperfine splitting constants are sufficiently different in magnitude that there is no overlap. This is not the case in reality, but we can assume it is as an exercise.

Each of the three pairs of chemically equivalent $I = \frac{1}{2}$ nuclei will split the signal into a triplet of relative intensities 1:2:1 (Table 13.2). Splitting a single line three times sequentially into 1:2:1 triplets produces the following pattern:



Adding up the number of lines with the same relative intensities results in 8 lines of intensity 1, 12 lines of intensity 2, 6 lines of intensity 4, 1 line of intensity 8, a total of 27 lines.

10. From Eqn. 13.2,

$$\mu_e = -g\beta S = 2.0023 (9.274 \times 10^{-21} \text{ erg/gauss}) \left(\frac{1}{2}\right) = 9.285 \times 10^{-21} \text{ erg/gauss}$$

$$E = \pm \mu_e H = \pm 9.285 \times 10^{-21} \text{ erg/gauss} (3.4 \times 10^3 \text{ gauss})$$

$= \pm 3.2 \times 10^{-17} \text{ erg}$, depending on alignment with the magnetic field.

Similarly, $E = \pm 7.6$ and $\pm 11.6 \times 10^{-17} \text{ erg}$

$$E = \frac{\pm 3.2 \times 10^{-17} \text{ erg/electron} (6.022 \times 10^{23} \text{ electrons/mole}) (10^{-7} \text{ J/erg})}{4.184 \text{ J/cal}}$$

$$= \pm 0.45 \text{ cal/mole}$$

Similarly, $E = \pm 1.1$ and ± 1.6 cal/mole

11. a) 2.5×10^{-5} moles/l (6.022×10^{23} molecules/mole) (1 spin/molecule) (l/1000 cm³)
= 1.5×10^{16} spins/cm³

b) Using Eqn. 13.15,

$$C_1 = \frac{h_1}{h_2} \frac{(\Delta H_1)^2}{(\Delta H_2)^2} (C_2)$$

$$C_{\text{unk}} = \frac{75}{60} \frac{(3.1)^2}{(2.5)^2} (2.5 \times 10^{-5} \text{ M}) = 4.8 \times 10^{-5} \text{ M}$$

12. Volume of solution analyzed = $\pi r^2 h = \pi d^2 h / 4$

Inner diameter of tube = 3 mm - 2(0.3 mm) = 2.4 mm = 0.24 cm

$$V = \pi (0.24 \text{ cm})^2 (4 \text{ cm}) / 4 = 0.18 \text{ cm}^3$$

a) # spins = 10^{-9} moles/l (0.001 l/cm³) (0.18 cm³) (6.022×10^{23} spins/mole)
= 1.1×10^{11} spins

b) absolute detection limit = 10^{-9} moles/l (0.001 l/cm³) (0.18 cm³) (200 g/mole)
= 3.6×10^{-11} g = 36 pg

c) 10^{-9} moles/l (0.001 l/ml) (200 g/mole) = 2×10^{-10} g/ml = 0.2 ng/ml

CHAPTER 14

1. For maximum sensitivity, the most suitable x-ray lines to measure would be Ta $K\alpha_{1,2}$ or Ta $L\alpha_{1,2}$. The Ta $K\alpha$ line, however, would require an x-ray generator capable of a power output greater than 60 kV in order to achieve maximum excitation efficiency, but has the advantage that Ta could be measured with no interference from Nb. Assuming that the Ta $L\alpha$ line is measured, then a LiF crystal and scintillation detector combination could provide the highest sensitivity because of the high reflectivity of LiF, and high efficiency of the scintillation detector at the Ta $L\alpha$ energy of 8.14 keV. Since niobium is present, the second order (i.e., $n=2$) Nb $K\alpha$ line would be diffracted at a 2θ angle of 43.59° using LiF(200), and would interfere with the Ta $L\alpha$ line at $2\theta = 44.42^\circ$. One could minimize or eliminate the interference by judicious choice of crystal and/or collimator combination. For example, higher order x-ray lines could be avoided through the use of a crystal which rejects second order reflections, such as the germanium crystal. However, the reflectivity of Ge is substantially less than that for the LiF crystal and hence sensitivity will be sacrificed. The best way to eliminate the interference is electronically by means of pulse-height selection. A modern commercial x-ray instrument is equipped with a pulse-height selector (PHS) which is designed to pass to the counting circuits only the pulse-height distribution that corresponds to the analyte line and to exclude all others. This is usually accomplished by selection of a baseline (lower level discriminator) to eliminate the detector and amplifier noise, and an upper level discriminator which determines the pulse energy band-width ("window-width") to be selected and counted. Since the pulse-height distributions for Ta $L\alpha$ and Nb $K\alpha$ would be centered about

different voltages because of their different x-ray line energies (e.g., $T_{L\alpha} = 1.52 \text{ \AA}$, $Nb_{K\alpha} = 0.78 \text{ \AA}$), appropriate selection of the baseline and upper level discriminators would achieve the maximum signal for Ta without interference from Nb.

2. The scintillation detector, generally speaking, is more efficient than the proportional detector at x-ray energies approximately 7-8 keV and is the detector of choice for measuring "hard" x-ray lines above this energy. Below 7 keV, the proportional detector is usually used for routine analysis because of its high efficiency. Therefore, the proportional detector would be used for $SiK\alpha$ and $U_{M\alpha}$, and the scintillation for $CuK\alpha$ and $IK\alpha$.

3. Assuming one measures the $PbL\alpha$ line (i.e., 10.55 keV), appropriate internal standards would be elements which are absent from the ore concentrate, and have absorption edge wavelengths close to the analyte line. Ideal elements would be Tl or Bi, if their x-ray lines could be resolved from the analyte line, e.g., $TiL\alpha = 10.27 \text{ keV}$ and $BiL\alpha = 10.84 \text{ keV}$. If spectral resolution is a problem, then Hg would be a good choice, e.g., $HgL\alpha = 9.99 \text{ keV}$. If the PbM line is measured, then the same criteria apply.

4. Using wavelength-dispersive XRF, potassium $K\alpha$ is easily resolved from the $ClK\alpha$ peak using appropriate crystal/collimator and PHS combination. With energy-dispersive XRF, a Si(Li) detector with a resolution at $MnK\alpha$ of at least 160 eV would be suitable for measuring $KK\alpha$ without peak overlap from the $ClK\alpha$. In the absence of any available standards, the sample could be fused with $Li_2B_4O_7$ to produce a glass disk. Standards could then be prepared by adding known amounts of K as KNO_3 or KCl , and SiO_2 if necessary, to the flux to produce synthetic glass disks. Another approach would be to dissolve the sample in HF and heat to volatilize the Si as SiF_4 , the residue could then be

taken up in dilute acid and passed through a cation exchange impregnated filter paper to quantitatively collect the K^+ ions. Suitable standards could then be prepared in a similar manner.

5. The thickness of zinc plating on an iron substrate can be determined by measuring the attenuation of the $Fe K\alpha$ line as described in Section 14.5 and can be calculated using Equation 14.21. Alternatively, standards can be prepared where known thicknesses of zinc are plated on an iron substrate. Calibration can be performed by a linear interpolation over the thickness region corresponding to the analyte sample thickness. For maximum accuracy, the interpolated region should bracket the analyte sample thickness.

6. Look up in a wavelength table the 2θ values which correspond to the first order $PuK\alpha$ and $PuL\alpha$ lines, respectively, for a particular diffraction crystal with known d spacing. Then, using Bragg's law, calculate $\lambda(\text{\AA})$ corresponding to each of these x-ray lines. Their energies can be calculated from the relationship $E_{\text{keV}} = 12.4/\lambda(\text{\AA})$.

7. In order to extend the analytical sensitivity of XRF methods to the ppm-ppb range, several preconcentration methods exist such as selective precipitation of the analyte elements followed by their collection on membrane filters, and ion exchange resin impregnated filter papers for collection of the analyte elements. Primary source of errors is the laboratory environment which includes vessels for dissolution of samples, and "dirty" reagent chemicals.

8. A Coolidge tube is an evacuated x-ray tube containing an anode of a particular target material and a heated (filament) cathode. The electrons emitted from the hot cathode are accelerated through a large potential drop of several thousand volts to the

anode. The impinging electron beam dislodges inner shell electrons from the target material, causing x-rays to be emitted as outer shell electrons drop down to the vacant orbitals.

9. An absorption edge is the wavelength corresponding to the energy required to just dislodge an inner shell electron and is therefore the longest wavelength that will dislodge the electron and be absorbed.

10. In x-ray fluorescence analysis, the sample is bombarded with x-rays from either an x-ray tube, radioisotopic source, or secondary target emitter. The sample need not be in a vacuum. Instrumental requirements are the x-ray source, an analyzing crystal and a detector for wavelength-dispersive analysis. The analyzing crystal is not used in energy-dispersive analysis but replaced by a high resolution Si(Li) detector and multi-channel analyzer. In x-ray absorption, the sample absorbs x-rays of an appropriate wavelength (near the absorption edge of the element of interest, if possible) and the absorption is a logarithmic function of the weight fraction of each component and their mass absorption coefficients. An x-ray source and a detector are required.

11. The nickel K_{α} line (doublet) occurs at 1.66 \AA and sodium chloride has a d of 2.82 \AA . Hence,

$$n\lambda = 2d \sin \theta$$

$$1 \times 1.66 = 2 \times 2.82 \sin \theta$$

$$\theta = 17^\circ 10' = 17.17^\circ$$

$$2\theta = 34.34^\circ$$

$$12. \lambda = 2d \sin \Theta = 2 \times 2.01 \sin \frac{69.36}{2}^\circ = 2.287 \text{ \AA} \quad (\text{convert degrees to radians})$$

From Table 14.1, this is the $K\alpha$ line of chromium.

$$13. \text{ From Eqn. 14.3, } \frac{hc}{\lambda_0} = Ve,$$

$$\lambda_0 = \frac{hc}{Ve} = \frac{(6.626 \times 10^{-34} \text{ J-sec})(2.9979 \times 10^8 \text{ m/sec})}{(50 \times 10^3 \text{ V})(1.602 \times 10^{-19} \text{ coul})}$$
$$= 2.48 \times 10^{-11} \text{ m} = 0.25 \text{ \AA}$$

14. Tabulated mass absorption coefficients at 1.54 \AA are $103 \text{ cm}^2/\text{g}$ for Cl, $4.52 \text{ cm}^2/\text{g}$ for C, and $0.48 \text{ cm}^2/\text{g}$ for H. The formula weight of carbon tetrachloride is 153.82. Therefore, in this compound:

$$x_{\text{Cl}} = \frac{4 \times 35.435}{153.82} = 0.922$$

$$x_{\text{C}} = \frac{12.011}{153.82} = 0.078$$

$$\mu_m(\text{CCl}_4) = 103 \times 0.922 + 4.52 \times 0.078 = 95.4 \text{ cm}^2/\text{g}$$

The formula weight of benzene is 78.114 and so

$$x_{\text{H}} = \frac{6 \times 1.0080}{78.114} = 0.077$$

$$x_{\text{C}} = \frac{6 \times 12.011}{78.114} = 0.923$$

$$\mu_m(C_6H_6) = 4.52 \times 0.923 + 0.48 \times 0.077 = 4.21 \text{ cm}^2/\text{g}$$

The mass absorption coefficient for the 1% by weight solution is

$$\begin{aligned}\mu_m &= \frac{1}{100} \times \mu_m(CCl_4) + \frac{99}{100} \mu_m(C_6H_6) \\ &= 0.01 \times 95.4 + 0.99 \times 4.21 = 5.12 \text{ cm}^2/\text{g}\end{aligned}$$

For 1 cm³ of solution in a cell of cross section 9.80 cm², the path length is 1/9.80 = 0.102 cm.

$$\log \frac{P_o}{P} = \frac{\mu_m l}{2.303} = \frac{5.12 \times 0.880 \times 0.102}{2.303} = 0.200$$

$$\frac{P_o}{P} = 1.58$$

$$T = \frac{P}{P_o} = \frac{1}{1.58} = 0.633$$

15. If the more intense peak is the K_{α} line of Si, then

$$n = 2d \sin \theta$$

$$\frac{n\lambda}{\sin \theta} = 2d$$

$$\lambda K_{\alpha} \text{ of Si} = 7.126 \text{ \AA}, n = 1$$

$$\text{then } 2d = \frac{(1)(7.126)}{\sin 54.605} = \frac{7.126}{0.8151} = 8.742$$

The crystal PET [Pentaerythritol Tetrakis (hydroxymethyl) methane] has a 2d spacing of 8.742.

Check this by calculating 2d for less intense peak at 101.16° . To what line does this correspond? (Answer: K_{β} line)

16. The amount of Ni^{2+} collected on SA-2 is

$$5.0/59 = 0.085 \mu\text{g}/\text{cm}^2$$

$$0.085 \mu\text{g}/\text{cm}^2 \times 14.5 \text{ cm}^2 = 1.2 \mu\text{g}$$

Concentration of Ni^{2+} in seawater =

$$\frac{1.2 \times 10^{-6} \text{ g}}{10^3 \text{ g solution}} = \frac{1.2 \times 10^{-9} \text{ g}}{\text{g solution}} = \frac{1.2 \text{ ng}}{\text{g}} \text{ or } 1.2 \text{ ppb}$$

Similarly, $\text{Mn}^{2+} = 2.2 \text{ ppb}$, and $\text{Zn}^{2+} = 5.0 \text{ ppb}$

17. Peaks 3 and 4 are FeK_α , FeK_β respectively; peaks 5 and 6 are CrK_α , CrK_β ; peaks 8 and 9 are NiK_α , NiK_β . Peak 1 is an escape peak produced by the excitation of Si in the detector by the CrK_α line. This requires 1.74 keV of the CrK_α energy. Therefore, the escape peak energy is $5.42 - 1.74 = 3.68 \text{ keV}$. Similarly, peak 2 is an escape peak produced by the FeK_α line at $6.40 - 1.74 = 4.66 \text{ keV}$. The escape peak produced by the NiK_α line is hidden under the lower energy side of the CrK_β line at 5.73 keV.

18. First obtain the respective influence coefficients by plotting the data. Since the NiK_α characteristic line energy lies just above the Fe K edge, the iron matrix will strongly absorb the Ni K_α characteristic radiation. Therefore, the effect of the Fe matrix on Ni analyte will be absorption and can be represented by the influence coefficient α_{NiFe} . A plot of $(W_{\text{Ni}}/R_{\text{Ni}}) - 1$ vs. W_{Fe} will be linear where the slope = $\alpha_{\text{NiFe}} = 1.71$. The effect of the nickel matrix on the iron analyte will be enhancement and the influence coefficient β_{FeNi} can be obtained by plotting

$$(W_{\text{Fe}}/R_{\text{Fe}}) - 1 \text{ vs. } \frac{W_{\text{Ni}}}{1 + W_{\text{Fe}}}$$

The slope of this linear plot will be

$$\beta_{\text{FeNi}} = -0.46$$

[Note that a plot of $(W_{\text{Fe}}/R_{\text{Fe}}) - 1$ vs. W_{Ni} is not linear.]

To calculate the weight fractions in the unknown sample, a successive approximation or iterative approach can be used as follows:

1st approximation: Let $W_{Fe} = R_{Fe} = 0.3172$

$$W_{Ni} = R_{Ni} = 0.5483$$

Therefore,

$$W_{Ni} = 0.5483 [1 + 1.71 (0.3172)] = \underline{0.8457}$$

$$W_{Fe} = 0.3172 [1 - 0.46 (\frac{0.5483}{1 + 0.3172})] = \underline{0.2565}$$

2nd iteration:

$$W_{Ni} = 0.5483 [1 + 1.71 (0.2565)] = 0.7888$$

$$W_{Fe} = 0.3172 [1 - 0.46 (\frac{0.8457}{1 + 0.2565})] = 0.2190$$

3rd iteration:

$$W_{Ni} = 0.5483 [1 + 1.71 (0.2190)] = 0.7536$$

$$W_{Fe} = 0.3172 [1 - 0.46 (\frac{0.7888}{1 + 0.2190})] = 0.2228$$

4th iteration:

$$W_{Ni} = 0.5483 [1 + 1.71 (0.2228)] = 0.7572$$

$$W_{Fe} = 0.3172 [1 - 0.46 (\frac{0.7536}{1 + 0.2228})] = 0.2273$$

5th iteration:

$$W_{Ni} = 0.5483 [1 + 1.71 (0.2273)] = 0.7614$$

$$W_{Fe} = 0.3172 [1 - 0.46 (\frac{0.7572}{1 + 0.2273})] = 0.2272$$

6th iteration:

$$w_{Ni} = 0.5483 [1 + 1.71 (0.2272)] = 0.7613$$

$$w_{Fe} = 0.3172 [1 - 0.46 (\frac{0.7614}{1 + 0.2272})] = 0.2267$$

7th iteration:

$$w_{Ni} = 0.5483 [1 + 1.71 (0.2267)] = 0.7608$$

$$w_{Fe} = 0.3172 [1 - 0.46 (\frac{0.7613}{1 + 0.2267})] = 0.2266$$

8th iteration:

$$w_{Ni} = 0.5483 [1 + 1.71 (0.2266)] = 0.7608$$

$$w_{Fe} = 0.3172 [1 - 0.46 (\frac{0.7608}{1 + 0.2266})] = 0.2267$$

Since the weight fractions no longer change after the seventh and eighth iteration, the final weight fractions are $w_{Ni} = 0.7608$ and $w_{Fe} = 0.2267$.

CHAPTER 15

1. By measurement of the peak positions with a ruler, the binding energies of the major peaks are interpolated to be 25, 103, 155, 285, 368, 375, and 535 eV. From comparison with Table 15.1, the following probable assignments can be made: Si 2p, 103 eV; C 1s, 285 eV; Ag 3d, 368 and 375 eV; O 1s, 535 eV. The 25 and 155 eV peaks cannot be matched to the binding energies listed in the table; consultation of more extensive tables indicates probable assignment to O 2s and Si 2s electrons.
2. By measurement of the peak positions with a ruler, the binding energies of the 6 apparent major peaks are interpolated to be 134, 161, 284, 403, 533, and 694 eV. By comparison to Table 15.1, the apparent assignments seem to be P 2p, S 2p, C 1s, N 1s, O 1s, F 1s, respectively. These are logical elements for an "organic" compound.
3. From Fig. 15.8, the binding energy of the Fe 2p_{3/2} photoelectron is approximately equal to 714 eV in Fe₂O₃ and 717 eV in FeF₂ (the non-argon-ion-sputtered spectrum A, in these two cases), and equal to 710 eV for pure Fe foil (the sputtered spectrum C, in which the presumed surface oxide has been removed). The whole range of "chemical shifts" is only about 7 eV. The elements around Fe, say V through Cu, average some 70 eV difference in binding energy with unit change in atomic number, about an order of magnitude larger than the "chemical shift."
4. See C. A. Evans, Jr., Anal. Chem., 47(9), 819A, 855A (1975).
5. a) and b) Assume that each Ag atom on the surface monolayer would occupy an area

roughly equal to its cross section, assuming a close-packed arrangement.

$$A_{\text{atom}} = \pi r^2 = \pi(1.44 \text{ \AA})^2 = 6.51 \text{ \AA}^2 = 6.51 \times 10^{-16} \text{ cm}^2$$

The entire surface area of a 1 mm diameter beam is

$$A_{\text{beam}} = \pi r^2 = \pi(d/2)^2 = \pi(0.5 \text{ mm})^2 = 0.785 \text{ mm}^2 = 7.85 \times 10^{-3} \text{ cm}^2$$

Then 0.001 of a monolayer coverage would be equal to the following number of silver atoms

$$n_{\text{Ag}} = (0.001) \frac{A_{\text{beam}}}{A_{\text{atom}}} = 0.001 \left(\frac{7.85 \times 10^{-3} \text{ cm}^2}{6.51 \times 10^{-16} \text{ cm}^2} \right) = 1.21 \times 10^{10} \text{ atoms}$$

About 10^{10} atoms of Ag.

$$\text{Mass of Ag} = \frac{1.21 \times 10^{10} \text{ atoms} (107.87 \text{ g/mole})}{6.022 \times 10^{23} \text{ atoms/mole}} = 2.16 \times 10^{-12} \text{ g Ag}$$

or about 2×10^{-12} g

c) The total analysis volume is that of a cylinder 1 mm in diameter and 20 Å high.

$$V = \pi r^2 h = \pi(0.05 \text{ cm})^2 (20 \times 10^{-8} \text{ cm}) = 1.57 \times 10^{-9} \text{ cm}^3$$

The concentration in g/cm³ is therefore

$$C = \frac{2.16 \times 10^{-12} \text{ g Ag}}{1.57 \times 10^{-9} \text{ cm}^3} = 1.38 \times 10^{-3} \text{ g/cm}^3 = 1.4 \times 10^{-3} \text{ g/cm}^3$$

Assuming the density of the material with only 0.001 monolayer of Ag is approximately equal to that of pure silicon

$$\text{ppm Ag} = (10^6) \left(\frac{1.38 \times 10^{-3} \text{ g Ag/cm}^3}{2.33 \text{ g/cm}^3} \right) = 5.9 \times 10^2, \text{ or about 600 ppm}$$

6. a) Al radiation is 1487 eV; the binding energy of the gold 4f_{7/2} electron is 83.8 eV.

Using Eqn. 15.3,

$$E_p = h\nu - E_b - E_{\text{wf}}$$

$$1353 \text{ eV} = 1487 \text{ eV} - 83.8 \text{ eV} - E_{wf}$$

$$E_{wf} = 50.2 = 50 \text{ eV}$$

For the C 1s peak at $E_b = 284 \text{ eV}$, $E_p = 1487 \text{ eV} - 284 \text{ eV} - 50 \text{ eV} = 1153 \text{ eV}$

b) Using Mg radiation of 1254 eV, the C 1s peak should be at

$$E_p = 1254 \text{ eV} - 284 \text{ eV} - 50 \text{ eV} = 920 \text{ eV}$$

7. From Table 15.1, the C 1s peak is at 284 eV, and O 1s is at 532 eV. Therefore, the peaks with binding energies at 290-300 eV are probably due to the C 1s photoelectrons for the three chemically different carbons in the three molecules. Because the E_b on a central atom would increase with increase in electron-withdrawing power of the substituents, the 290.1 peak is probably due to CH_4 , 295.8 to CO, and 297.9 to CO_2 . The peaks at about 540 eV are probably O 1s photoelectrons. The O in CO can probably pull more electron density to itself than each O in CO_2 , therefore the peak with lower binding energy (540.1 eV) is probably O 1s in CO; and 541.3 eV for O 1s in CO_2 .

8. From Table 15.1, the two peaks are probably due to the Al 2p photoelectrons; the peak at lower binding energy to Al^0 , that at higher binding energy to Al^{3+} . Aluminum metal is well known to form a thin protective skin of Al_2O_3 very quickly. Even short exposure to air following abrasion allowed some Al_2O_3 to form. A full week's exposure to air allowed a thicker skin to form (relative increase in the peak of higher E_b), although the oxide skin must still be less than about 20 Å, or it is not 100% Al_2O_3 , because photoelectrons from the underlying Al^0 are still seen.

9. Plotting the count ratio as a function of % MoO_2 produces a plot that appears quite linear from 5 to 100% MoO_2 . Using this as a calibration curve, the count ratios for the three unknowns result in 83, 68, and 30% MoO_2 for the unknowns. Putting a

linear-least-squares line through these 14 points on the calibration curve results in 83.3, 68.1, and 30.0% MoO_2 .

10. From the top spectrum (1254 eV excitation energy), the measured kinetic energies of the photoelectrons are approximately (given the accuracy possible by measurement with a ruler) 168, 300, 321, 1137, and 1190 eV for peaks labeled L_I , L_{II} , L_{III} , M_I , $M_{II,III}$, respectively. By use of Eqn. 15.1, the binding energies are obtained by subtracting the measured kinetic energies from the 1254 eV of the incident photon, resulting in approximately 1086, 954, 933, 117, and 64 eV for binding energies.

In a similar manner, binding energies of approximately 1102, 955, 930, 112, and 68 eV are obtained from the lower spectrum which used 1487 eV excitation.

Note that the two sets of calculated binding energies are, within measuring error, the same, as would be expected. The measured kinetic energies change because of the different exciting line, but the binding energies should be constant.

The energies of the peaks labeled L_{II} and L_{III} (about 954 and 932 eV) correspond most closely to the 951 and 931 eV listed in Table 15.1 for the $2p_{1/2}$ and $2p_{3/2}$ electrons of Cu. This is also consistent with nomenclature rules for the two systems: a 2s electron would be in the L_I shell, etc.

CHAPTER 16

1. It is preferred to use MKS units for these calculations. Express 30.00 cm as 0.300 m. The M^+ of methane (mass 16) has a mass per molecule of $0.016 \text{ kg} / 6.02 \times 10^{23} \text{ molecules}$ or $2.66 \times 10^{-26} \text{ kilograms}$. The unit of charge is $1.6 \times 10^{-19} \text{ coulombs}$.

$$m/z = \frac{B^2 r^2}{2V}$$

$$B = \sqrt{\frac{2Vm}{zr^2}}$$

$$B = \sqrt{\frac{2 \times 3000 \times 2.66 \times 10^{-26}}{1.6 \times 10^{-19} \times (0.300)^2}} = 0.105 \text{ tesla}$$

0.105 tesla = 1.05 kilogauss or 1050 gauss

The radius of trajectory of m/z 15 (CH_3^+)

$$r = \sqrt{\frac{2Vm}{zB^2}} = \sqrt{\frac{2 \times 3000 \times 2.49 \times 10^{-26}}{1.6 \times 10^{-19} \times (0.105)^2}} = 0.291 \text{ m}$$

$r = 29.1 \text{ cm}$

$$2. B = \sqrt{\frac{2Vm}{zr^2}} = \sqrt{\frac{2 \times 3000 \times 2.13 \times 10^{-25}}{1.6 \times 10^{-19} \times (0.300)^2}}$$

$B = 0.298 \text{ tesla} = 2980 \text{ gauss}$

Calculating the radius of the m/z 127, we obtain 29.9 cm. We can see that the difference in radii for m/z 127 and 128 is approximately 0.1 cm, compared to approximately 0.9 cm for m/z 15 and m/z 16. Thus, the factor of about 9 in mass resolution is necessary to separate $M-H^+$ and M^+ for napthalene, compared to $M-H^+$ and

M^+ for methane (which should be the ratio of their masses).

3. Since $m/z = B^2 r^2 / 2V$, we can write that $m_1/m_2 = V_2/V_1$; $V_2 = V_1(m_1/m_2) = 3000$ (500/850); $V = 1765$ V. The accelerating voltage must be reduced from 3000 V to 1765 V (by using a voltage divider).

4. Chamber: +1765 V; exit slit: ground; repellers: 1775 V; filament: 1715 V; target: 1845 V; see Figure 16.3.

5. Similar to Problem 3, we can write $m_1/m_2 = V_2/V_1$ or $218.9856/m_2 = 0.99463$ $V_1/1.00000 V_1$

$$m_2 = 220.1679$$

The best match is 220.1674, which corresponds to $C_{11}H_{24}O_4$. Note, perfect agreement is not expected because of errors in the voltage divider used to reduce V_1 to 99.463% of its value.

6. $\Delta m = 28.0313 - 27.9949 = 0.0364$

$$R = m/\Delta m = 28/0.0364 = 770$$

for CO and C_2H_4 . Note that m was taken as the nominal mass; to be absolutely correct, we should use the mean of the two masses to be separated.

For the second set: $\Delta m = 0.0364$

This difference can be computed by adding up the exact masses (use tables of physical atomic masses), or by noting that the two formulas differ by a CO vs. C_2H_4 .

$$R = 280/0.0364 = 7,700$$

Because the mass is ten times greater, the resolution requirement is as well. Note that it becomes increasingly difficult to separate two molecular ions, differing by the

same groups of atoms, as the mass increases.

7. Again, use MKS units for this calculation. Starting with C_6H_6 (m/z 78):

$$t = L/(2Vz/m)^{\frac{1}{2}}$$

$$t = 1.0 \text{ m} / (2 \times 3000 \times 1.6 \times 10^{-19} / 1.26 \times 10^{-25})^{\frac{1}{2}}$$

$$t = 1.15 \times 10^{-5} \text{ sec or } 11.5 \mu\text{sec for m/z 78}$$

Similarly, we calculate for C_2H_2 :

$$t = 0.67 \times 10^{-5} \text{ sec or } 6.7 \mu\text{sec for m/z 26}$$

and for $C_6H_5^+$:

$$t = 11.4 \mu\text{sec for m/z 77}$$

8. Again use MKS units: 7,800 gauss = 0.78 tesla

$$\omega = \frac{zB}{m} = \frac{1.6 \times 10^{-19} \times 0.78}{1.29 \times 10^{-25}}$$

$$\omega = 9.67 \times 10^5 \text{ radian/sec}$$

Now, $2\pi f = \omega$, where f is cycles per sec (Hertz).

$$f = 0.67 \times 10^5 / 3.14 \times 2$$

$$f = 1.53 \times 10 = 153 \text{ kilohertz}$$

9. a) For C_6H_6 : $\frac{M+1}{M} = 0.011N$, where N = the number of carbon atoms

$$\frac{M+1}{M} = 0.066 \text{ or } 6.6\%$$

$$\frac{M+2}{M} = \frac{(1.1N)^2}{200} = 0.22\%$$

b) For $C_2H_4O_2$: $M+1/M = 2.2\%$

$$(M+2)/M = (2.2)^2/200 + 2(0.2\%) = 0.41\%$$

Recall that the abundance of O-18 is 0.2% if O-16 is considered to be 100%.

c) For $C_2H_8N_2$: $(M + 1)/M = 2.2\% + 2(0.036\%) = 2.9\%$

$$(M + 2)/M = (2.2)^2/200 = 0.02\%$$

d) For C_3H_7Cl : $(M + 1)/M = 3.3\%$

$$(M + 2)/M = (3.3)^2/200 + 32.5 = 33\%$$

$$(M + 3)/M = 33 \times 0.033 = 1.1\%$$

e) For C_2H_4S : $(M + 1)/M = 4.4\% + 0.80\% = 5.2\%$

$$(M + 2)/M = (4.4)^2/200 + 4.4\% = 4.5\%$$

f) For $C_{16}H_{34}$: $(M + 1)/M = 16 \times 1.1\% = 17.6\%$

$$(M + 2)/M = (17.6)^2/200 = 1.5\%$$

10. From the Handbook of Chemistry and Physics

Hg - 196	0.16
Hg - 198	10.02
Hg - 199	16.92
Hg - 200	23.10
Hg - 201	13.22
Hg - 202	29.72
Hg - 204	6.84

Now $Hg(CH_3)_2$ will have an $M + 1$ of $0.022 \times M$

<u>Composition</u>	<u>m/z</u>	<u>Intensity</u>	<u>Rel. Int.</u>
$^{196}Hg(CH_3)_2$	226	0.16	0.16
$^{196}Hg(^{13}CH_3)(CH_3)$	227	0.003	0.003
$^{198}Hg(CH_3)_2$	228	10.02	9.61
$^{199}Hg(CH_3)_2$ and $^{198}Hg(^{13}CH_3)(CH_3)$	229	16.92 + 0.22	16.77
	230	23.10 + 0.37	22.57
	231	13.22 + 0.51	13.43

232	29.72 + 0.29	29.37
233	0.65	0.64
234	6.84	6.67
235	0.15	0.15

Note that many organometallics have characteristic isotope cluster patterns for the molecular ion which can be used to prove the presence of the metal atom in the molecule.

11. We start with m/z 121 because we know it's C_8H_7DO only. We next correct the intensity at m/z 122 for the C-13 contribution from m/z 121: $0.088 \times 4.42 = 0.39$. The corrected intensity at 122 is $7.01 - 0.39 = 6.62$. Moving to m/z 123: the corrected intensity is $100.00 - 6.62 \times 0.088 = 99.42$. Finally, m/z 124: $8.75 - 0.088 \times 99.42 = 0.00$ (this is only a C-13 peak).

$$d_1 = 4.42 = 4.0\%$$

$$d_2 = 6.62 = 6.0\%$$

$$d_3 = \underline{99.42} = \underline{90.0\%}$$

$$110.46 \quad 100\%$$

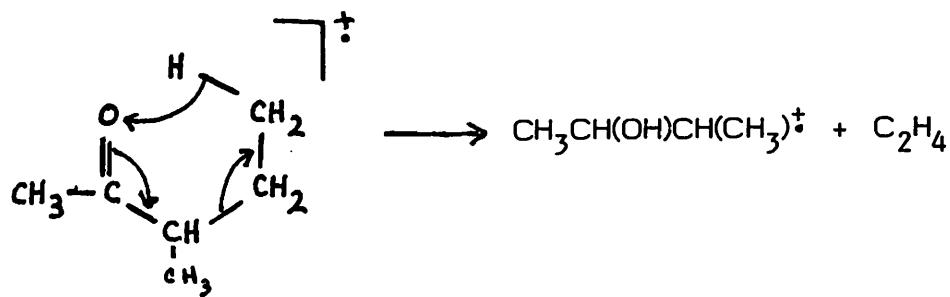
12. The molecular ion is 112 and contains six carbons (from the $M + 1$ intensity). The intense $M + 2$ signals the presence of chlorine. Therefore, the elemental composition is C_6H_5Cl . Note the intense 77 ($C_6H_5^+$), 51 ($C_4H_3^+$), 39 ($C_3H_3^+$) which signals a phenyl group. The signals at half masses are doubly charged ions often found in aromatic compounds. Note that the intensity of m/z 113 is enhanced by an $M-H$ from the 114 (compare m/z 111 and 112). Answer: Chlorobenzene.

13. Recall that the nitrogen atom will direct the α -bond to cleave: $R_2N-CH_2 \overset{\beta}{\text{C}} R$, and that the larger alkyl groups are preferentially lost. The molecular ion is m/z 73. It

preferentially loses C_2H_5 along with some methyl and less H. Answer: $\text{CH}_3\text{CH}_2(\text{CH}_3)\text{CHNH}_2$ (sec-butylamine). The compound cannot be methyl-n-propylamine because this material would give insignificant CH_3 loss.

14. The molecular ion is 144 and the strong peak at 146 indicates the presence of one bromine atom in the molecule. Note that $144 \rightarrow 127$, a loss of 17, which is OH. The loss of 16 must be O. Presumably $127 \rightarrow 116$, another loss of oxygen. Answer: HBrO_4 (perbromic acid).

15. Ketone #1 is probably a methyl ketone: note the m/z 43 peak which has 2 carbons, i.e., CH_3CO^+ . Supporting evidence is the loss of methyl; although weak, it's expected to be since the larger alkyl is lost from a molecule $\text{CH}_3\text{COC}_4\text{H}_9$. The next question is: What is the C_4H_9 ? Note the intense even mass ion at 72 (loss of C_2H_4). This can only arise from a molecule in which C_4H_9 is sec-butyl; i.e.,



Ketone #2 is not a methyl ketone: m/z 43 is C_3H_7^+ (note the m/z 44: m/z 43 ratio). Also note there are no abundant even mass ions. The ketone loses ethyl and propyl abundantly. The propyl group cannot be n-propyl, otherwise a McLafferty rearrangement would give loss of 28 (C_2H_4). Answer: Ketone #2 is ethyl-iso-propyl ketone.

16. The molecular ion is m/z 136. It contains nine carbons (note the ratio of intensities for m/z 137 : m/z 136). Therefore, the formula must be $\text{C}_9\text{H}_{12}\text{O}$. The base peak at m/z 94

is an odd electron ion (even mass) which comes from a rearrangement. The formula of m/z 94 is C_6H_6O or $PhOH$. The fragment lost is $C_9H_{12}O-C_6H_6O=C_3H_6$. Therefore, the molecule is $PhOC_3H_7$. Now, we must assign C_3H_7 : is it n-propyl or iso-propyl? If it's n-propyl, we expect some loss of C_2H_5 : $PhOCH_2\overset{+}{C}H_2CH_3$. If it's iso-propyl, we expect the loss of CH_3 to be greater than CH_3 -loss: $PhOCH-\overset{+}{C}H_3$.

We see that there is little m/z 121 and some m/z 107. Answer: Phenyl-n-propyl ether.

17. From a table of exact masses we find O = 15.9949 and S = 31.9721. $O_2 = 31.9898$. The difference in mass is $31.9898 - 31.9721 = 0.0177$. $R = m/\Delta m = 32/0.0177 = 1810$. At mass 320, two organic molecules which differ in that one has two oxygens and the other a sulfur, a resolution of 18,100 would be required.

18. Recall that the mass of a metastable ion is given by $m^* = m_2^2/m_1$. We can answer this question by inspection, since we know neither m_2 nor m_1 . Consider $32 \rightarrow 31$ ($m^* = 31^2/32 = 30.03$). How about $32 \rightarrow 30$ ($m^* = 28.13$)? Consider $31 \rightarrow 29$ ($m^* = 27.13$). This is a perfectly reasonable situation. That is, the molecular ion loses H to give 31, which in turn, loses a neutral molecule H_2 , an expected process for an even electron ion (even electron ions tend to lose neutral molecules, rather than radicals, to give other even electron ions).

19. A. Process (a) is $45 \rightarrow 19$; $m^* = 19^2/45 = 8.02$. Process (b) is $45 \rightarrow 29$; $m^* = 18.7$. B. Rephrasing the question: which molecule gives a $C_2H_5O^+$ which would not give a favorable expulsion of H_3O^+ ? Answer: $C_2H_5O^+$ with a center oxygen; i.e., $CH_3O=CH_2^+$. The precursor structure must be CH_3OCH_2Y .

20. Write the structure of the two isomers. The 2,2,4-isomer is $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$. The 2,3,4 is $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}_3$. Remember we expect cleavages to occur at the branch point. The 2,2,4 should cleave to give $\text{CH}_3\text{C}(\text{CH}_3)_2^+$ or m/z 57 as the base peak. That's isomer "a". The 2,3,4-isomer should cleave at the center carbon to give $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)^+$, $\text{C}_5\text{H}_{11}^+$ or m/z 71. That's isomer "b."

21. Since the molecule contains nitrogen, we might expect the molecular ion to have an odd mass: m/z 73 is a good candidate. If that is true, the molecular formula may be $\text{C}_4\text{H}_{11}\text{N}$. The ion at m/z 58 clearly has three carbons and one nitrogen (consider the m/z 59 intensity). Therefore, m/z 58 is $\text{C}_3\text{H}_8\text{N}$, which confirms the molecular ion formula assignment. We are dealing with a saturated amine which can undergo a facile loss of CH_3 and no C_2H_5 loss (look at m/z 44). The two candidates are diethylamine, methyl-iso-propylamine, and t-butylamine. The first two candidates should give some loss of H (each have four H-atoms situated for α -cleavage). Yet, none is observed. Answer: t-butylamine.

22. All we need to do is normalize the relative intensities so that M has an intensity of 100%. $\text{M: M + 1: M + 2} = 18.5: 1.15: 0.074 = 100: 6.2: 0.40$. The best match is with that for $\text{C}_5\text{H}_{10}\text{O}$. The other candidate is $\text{C}_5\text{H}_{12}\text{N}$, but this is a fragment ion, not a molecular ion. We should ask why the agreement isn't any better. Both M + 1 and M + 2 are weak peaks which are subject to measurement errors and interferences. Interferences presumably enhance the relative intensities for M + 1 and M + 2. This happens often in mass spectrometry. The lesson is: do not accept without question M + 1 and M + 2 relative abundances. They are but one piece of information in a mass spectrum.

23. Simply calculate the exact masses:

CO	= 15.9949 + 12.000	= 27.9949
N ₂	= 2 x 14.0031	= 28.0062
C ₂ H ₄	= 24.0000 + 4 x 1.0078	= 28.0312

Scanning from low to high mass, the order would be CO, N₂, and C₂H₄.

CHAPTER 17

1. a) A diluent is an inert material mixed with a sample to increase its mass or change its thermal characteristics. Used in TG, DTA and DSC.
 - b) Thermal conductivity is the measure of a material's ability to conduct heat.
 - c) Heat capacity is the quantity of heat required to raise the temperature of a quantity of a material by 1°C. The quantity of the material involved may be expressed in any convenient units, e.g., moles, grams, etc.
 - d) Pyrolysis is the destruction of organic matter by heat in the absence of oxygen.
 - e) Plots of DTA data are called thermograms, as defined by IUPAC.
 - f) Dynamic atmosphere refers to a flowing gaseous environment in any thermal analysis technique. This flowing gas may be of constant or varying composition.
2. Heat is a form of energy. Temperature is an indirect measure of the amount of energy a system has. Changes in the amount of heat in a system and the system's temperature are directly related through the heat capacity of the system.
3. Since $\Delta G = \Delta H - T\Delta S$, and since the melting of any substance is a state change only ($\Delta G = 0$) where the entropy always increases, then $\Delta H = T\Delta S$. Since the $T\Delta S$ term is always positive, the process is always endothermic.
4. a) One may view this problem from either an equilibrium or a kinetic standpoint.

EQUILIBRIUM

The equilibrium constant is $K_{eq} = [\text{gas}][\text{product}]/[\text{reactant}]$. This varies with temperature, usually increasing for this type of reaction. If there is no gas in the system, then the maximum amount of product can be formed at equilibrium. Increasing the amount of gas present decreases the amount of product at that temperature. The effect appears as a delay in the onset of reaction. A similar argument applies if the gas is the reactant, with the conclusion that increased gas concentrations hasten the start of the process.

KINETIC

The rate of decomposition may be stated as $\text{RATE} = k [\text{reactant}] - k [\text{gas}] [\text{product}]$. Since the start of the reaction occurs when sufficient mass has been lost to observe a mass change, it will be delayed if the gas concentration is elevated. Similarly, the rate of mass change will decrease compared to the case where no gas is present. In the analogous situation where the gas is one of the reactants, then the rate is increased and mass changes are observed sooner.

b) Using the kinetic case as an example, one may determine apparent rates from the slope of a TG curve. A plot of $\log \text{RATE}$ versus $\log [\text{GAS}]$ will give a plot with a slope of n , the exponent of the gas term.

NOTE: This discussion used TG as an example. Virtually no change is needed in applying it to DTA or DSC experiments also.

5. A change in heat capacity with temperature is indicative of a heat of reaction which is not constant with temperature. Similarly, $\ln \Delta G$ and ΔS will no longer vary as expected with temperature.

6. See Table 17.2 and related text.

7. As a sample decomposes, gases may be evolved. If these gases remain near the

sample, this self-generated atmosphere will replace the experimental atmosphere. Since this self-generated atmosphere is a reaction product, it will usually decrease reaction rates and increase reaction temperatures. Dynamic atmospheres are used to reduce this problem.

8. Very slow reactions may not be observable by thermal analysis. These reactions may have significant effects over long time periods.

9. The number of variables which must be controlled, the length of the experiment and the expense of the instrumentation all suggest that another method be used for routine analyses such as these.

10. Melting (fusion), a crystal structure change, or decomposition to non-volatile products are the three possible processes. Tables in the text suggest which should be endothermic.

11. Looking at the plots of data from both methods, one finds that they both have the same abscissa. However, TA has an ordinate of temperature while DTA has one of temperature difference. This gives DTA an expanded scale for the ordinate and small thermal effects may be readily seen.

12. This is a case where the sample is super-cooled before crystallization. It is not a rare occurrence in thermal analysis.

13. The glass state is considered to be similar to the liquid state without its fluidity. The crystalline state indicates an orderly arrangement of molecules where the glass state

is disordered as in liquids. Polymers obtain many of their characteristics from the proportion of crystalline and glass character present. Since dissolution or even grinding may disrupt this character, thermal methods are preferred since little or no pretreatment is required for analysis.

14. Among other possibilities are (1) polymer characterization, (2) rapid heat capacity measurements, and (3) rapid estimates of thermal stability.

15. The basic problem with this type of analysis is in obtaining a valid (micro) sample from a very heterogeneous mixture. This applies to many other "natural" samples.

16. Some areas for computer applications are (1) peak area measurement, (2) instrument control, (3) data gathering and calculations, (4) baseline corrections, (5) automated decomposition temperature calculations.

17. In both cases, the major reaction is $H^+ + OH^- \rightarrow H_2O$. This drives the reaction, overshadowing the weak ionization of the acid itself.

18. The volume of the reactant solution determines the heat capacity and the moles of product which may be formed and therefore the heat released by the reaction. Thus, the decrease in heat capacity of a system will exactly parallel the decrease in the amount of heat produced by a smaller system, and the temperature change observed will be the same for large and small systems.

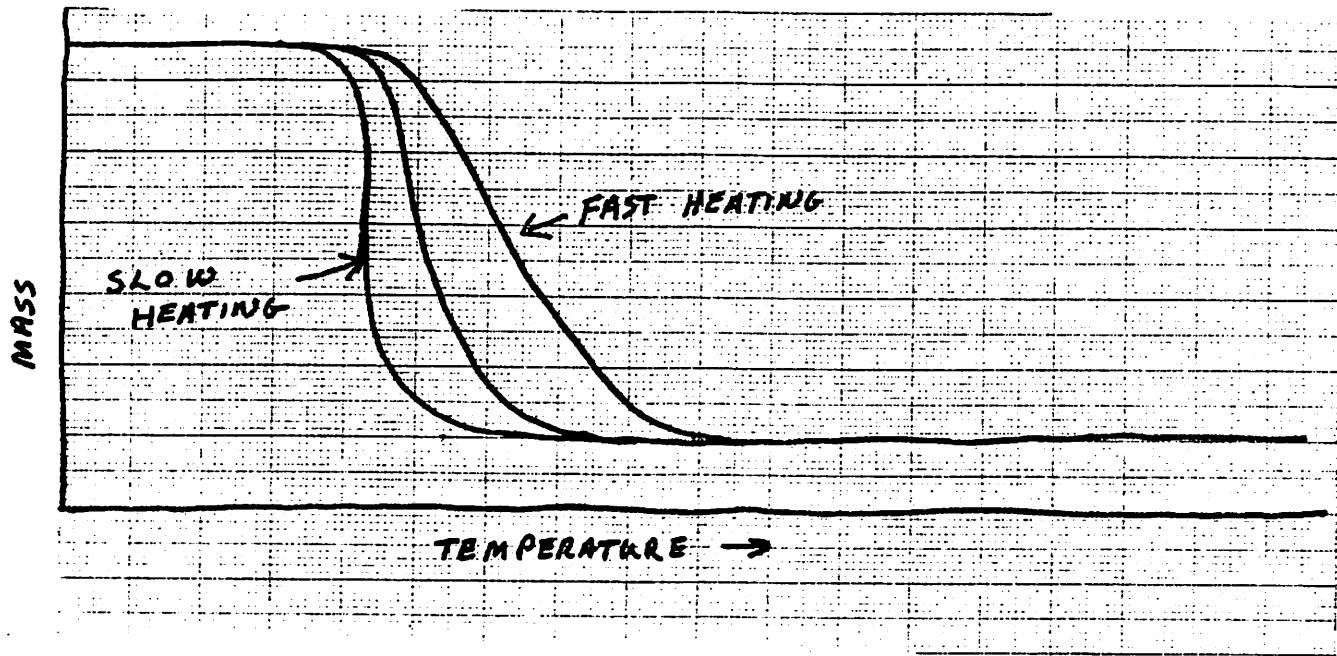
If the calorimeter cell, temperature measuring device and other components are included in the calculation, then the heat capacity will decrease at a slower rate than the amount of heat generated if the system is made smaller. At the same time, the relative

surface area increases, thus increasing heat loss to the surroundings. The conclusion is that decreasing calorimeter size has no advantage unless it may be related to cost or availability of the reactants to be studied.

19. A slow reaction will tend to give a late end point. This will result in an overestimate of the concentration of the analyte.

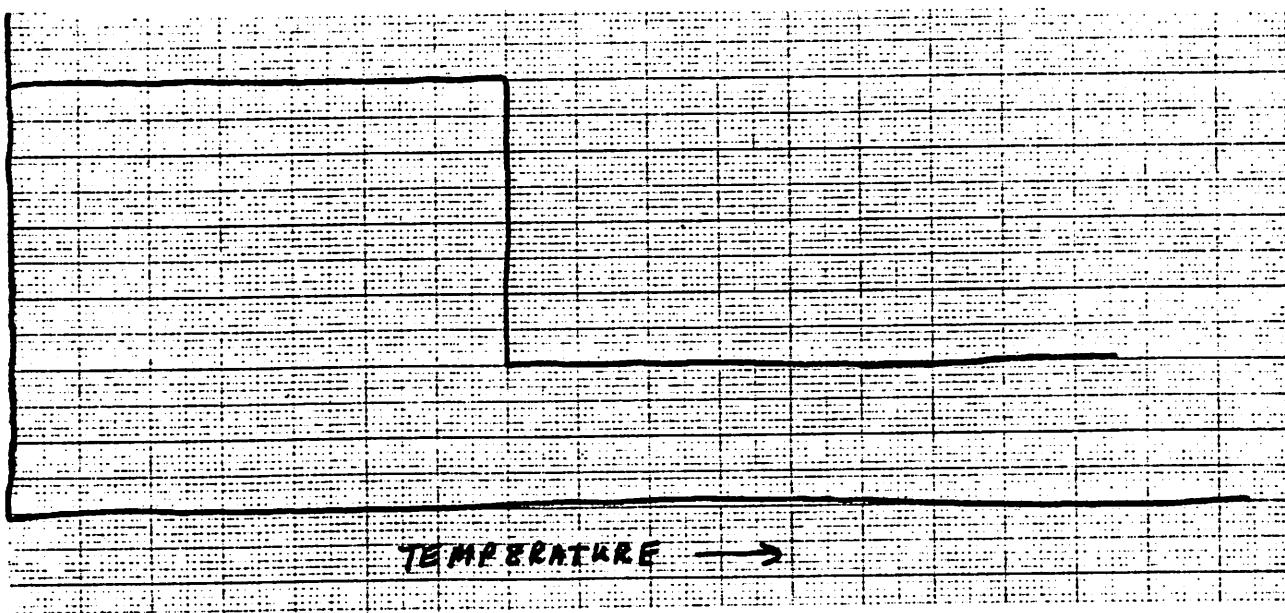
20. Among others, these include (1) weak acid or base reactions, and (2) reactions in cloudy or deeply colored mixtures.

21.



22.

MASS



The ideal decomposition curve would occur instantaneously, resulting in a step-like curve, provided that the product gases are removed.

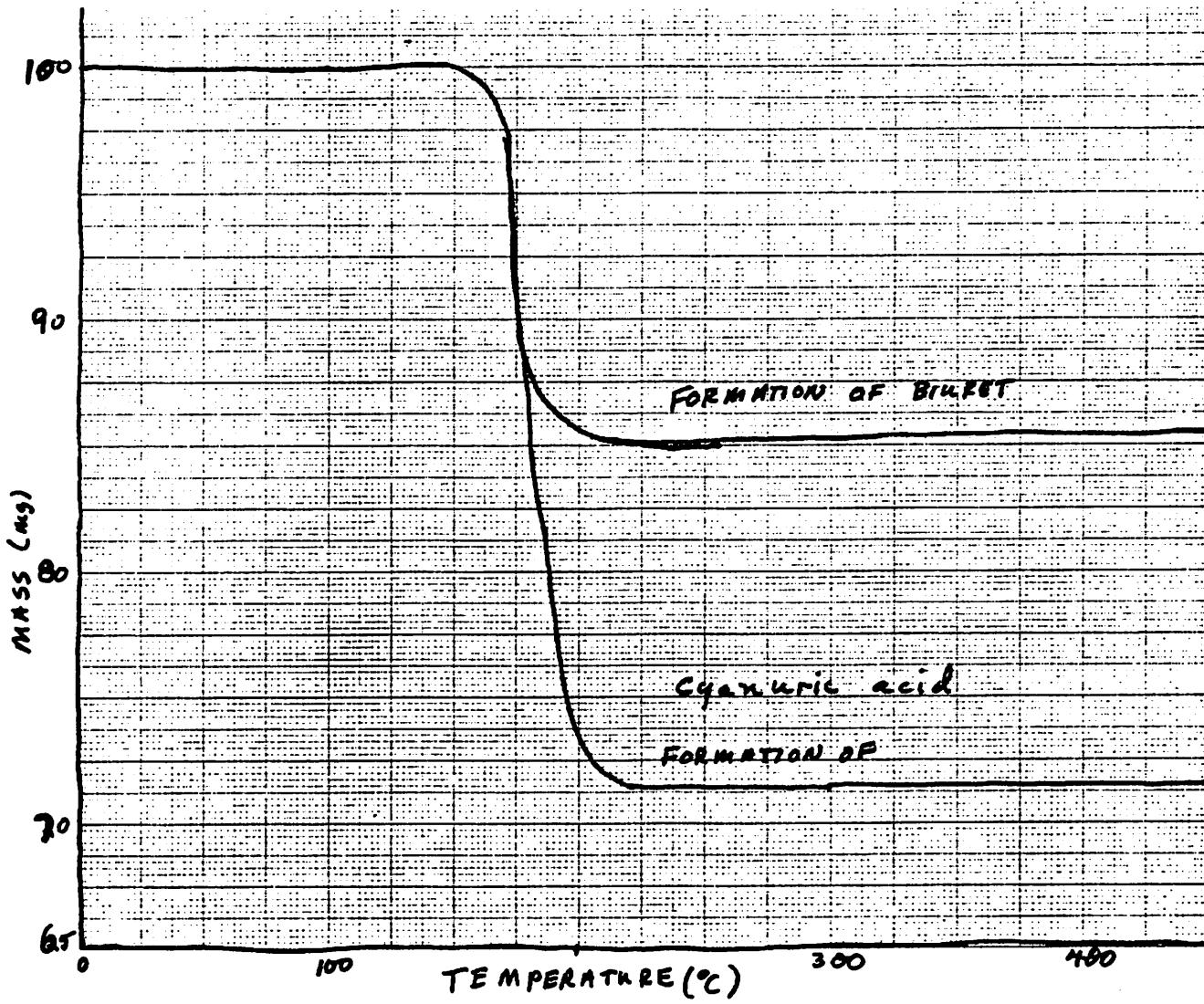
23. The reactions and masses involved are (NOTE: Urea sublimes and this experiment is difficult):



(100 mg) (85.8 mg) (14.2 mg)



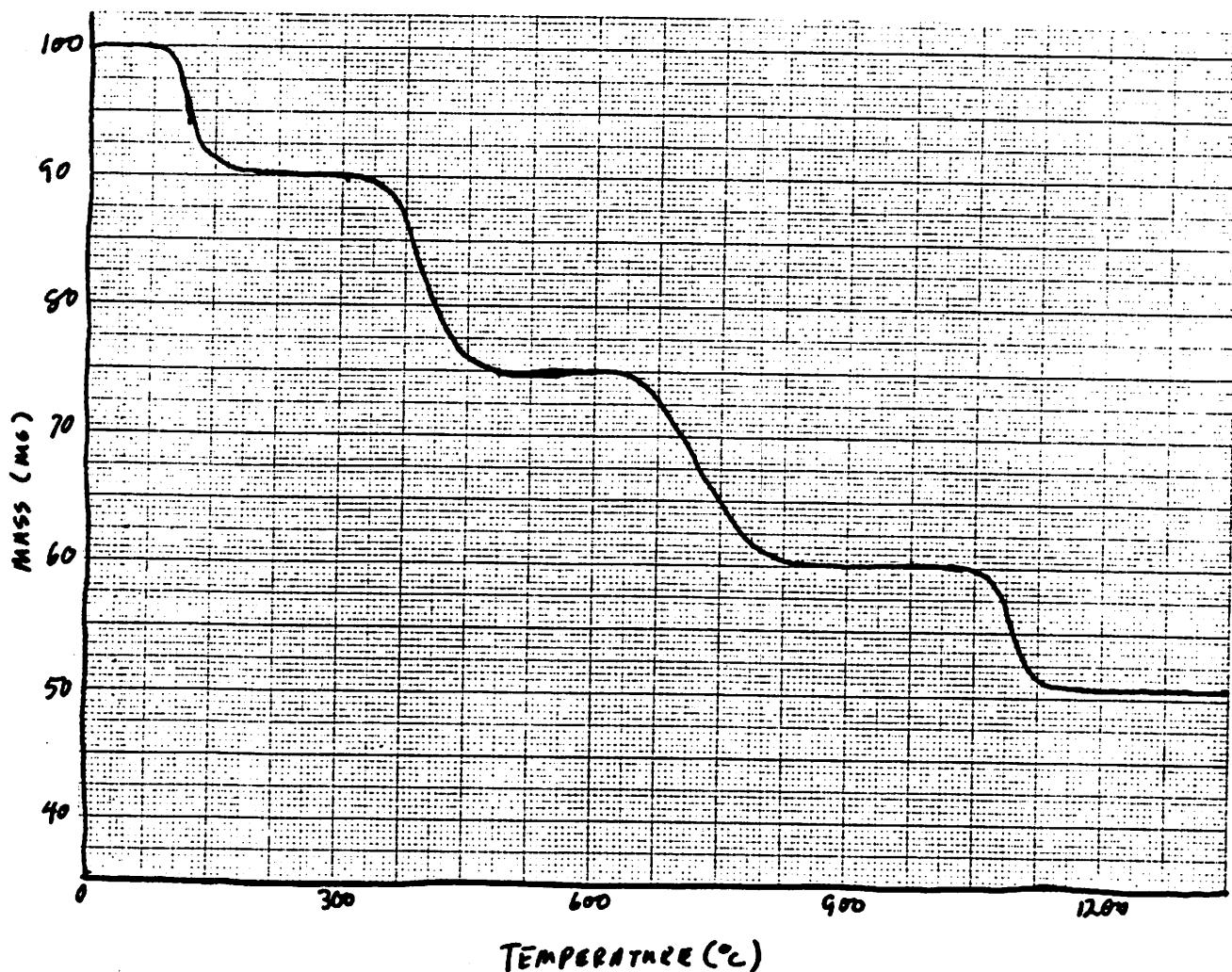
(100 mg) (71.7 mg) (28.3 mg)



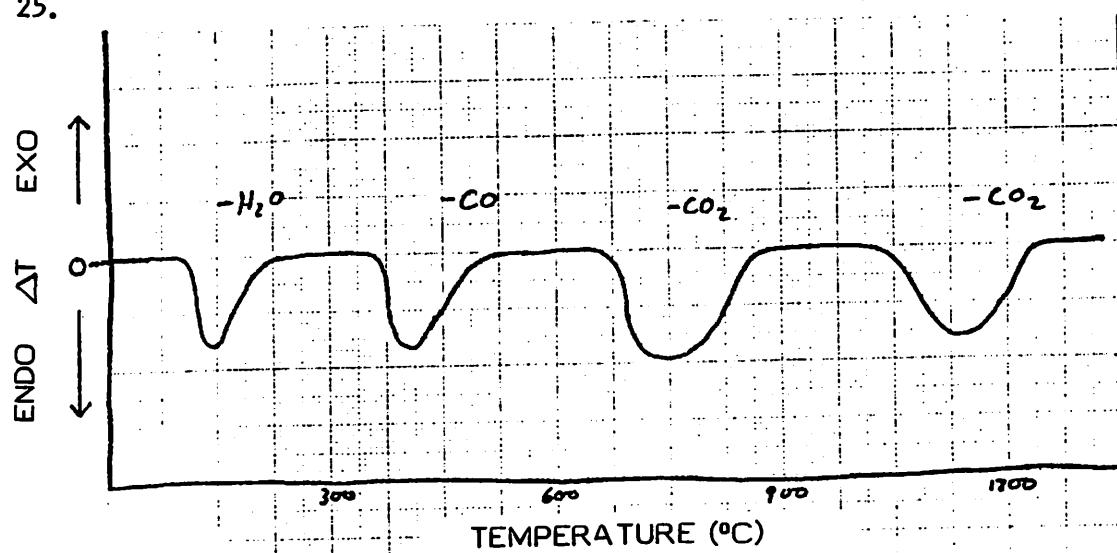
17-123

24. The data for this problem are:

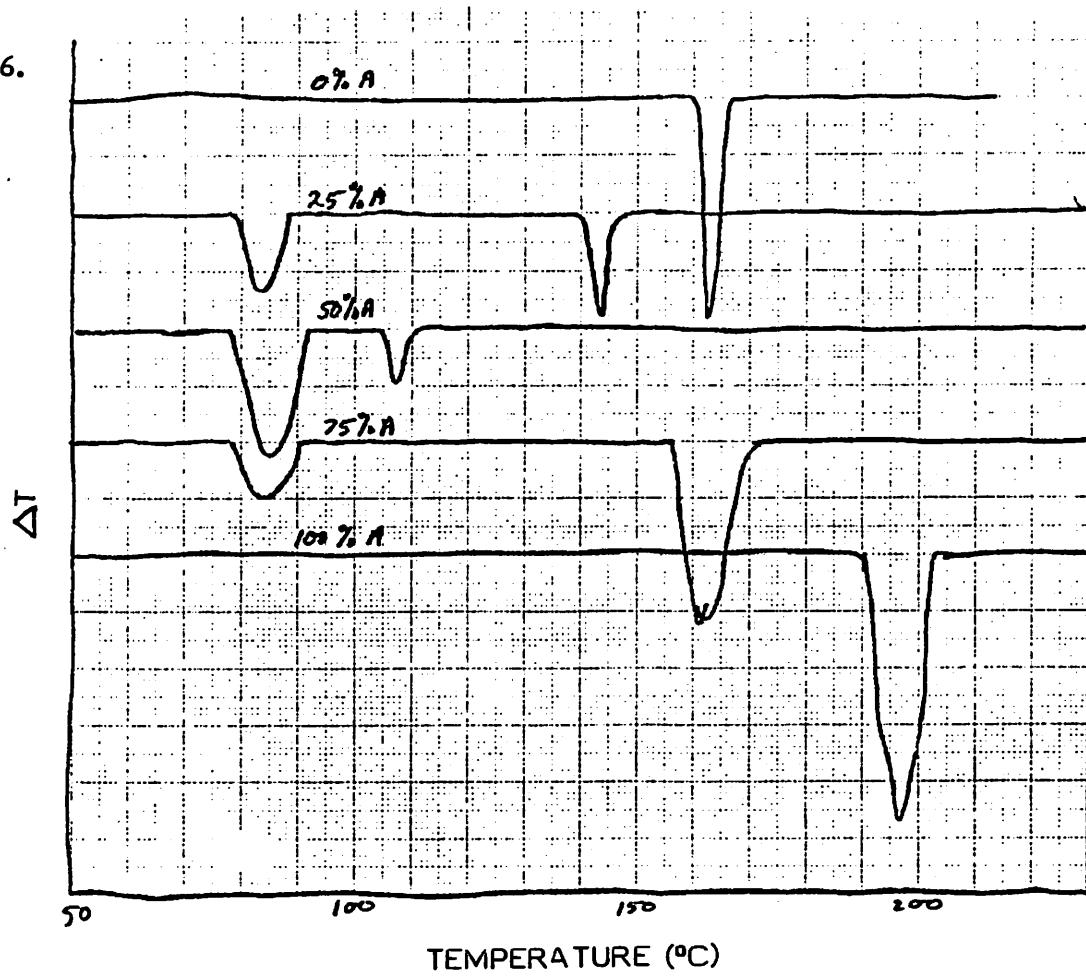
REACTION	MASS CHANGE	TEMP. RANGE, °C
$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$	- 6.16 mg	100-250
$\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$	- 9.59 mg	360-500
$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	-15.07 mg	620-960
$\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{BaC}_2\text{O}_4 + \text{H}_2\text{O}$	- 3.70 mg	100-250
$\text{BaC}_2\text{O}_4 \rightarrow \text{BaCO}_3 + \text{CO}$	- 5.76 mg	360-500
$\text{BaCO}_3 \rightarrow \text{BaO} + \text{CO}_2$	- 9.05 mg	above 1100



25.



26.

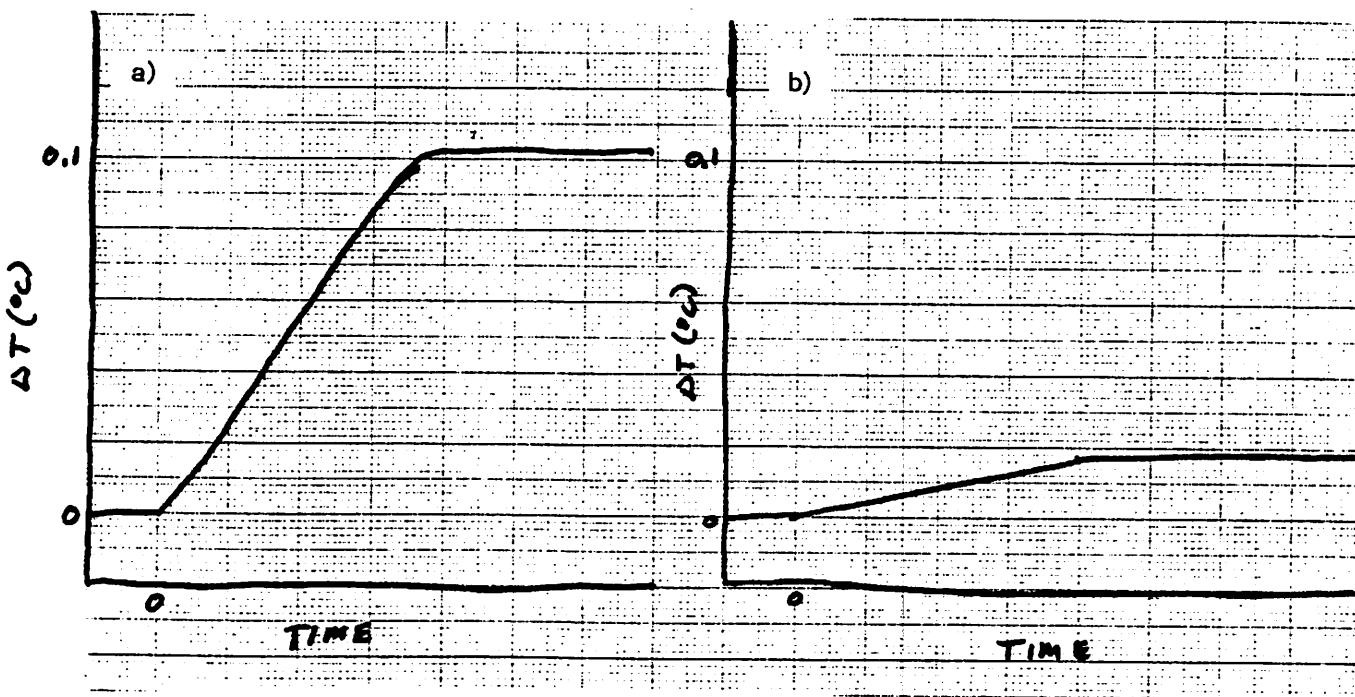
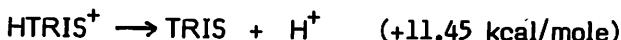


27. The heat of ionization refers to the reaction:



a) Titration of TRIS with H^+ is the reverse of this reaction and the heat of reaction is -11.45 kcal/mole (curve a)

b) Titration of the salt HTRIS⁺ with base is the combination of (curve b):



c) Temperature changes may be estimated by assuming a heat capacity due only to the solutions mixed. For the first reaction, the total heat capacity is 50.5 cal/ $^{\circ}\text{C}$ and the temperature change is approximately 0.113°C . In the second case, a temperature change of approximately 0.0186°C is expected.

28. The weight loss is equivalent to 0.517 mmoles of H_2O ; the remaining weight represents 0.251 mmoles of salt. There are two waters of hydration in this salt.

29. The salt left may be CuCl_2 , which is 0.106 mmoles. The mass loss is ammonia and represents 0.635 mmoles of NH_3 . The formula is $\text{Cu}(\text{NH}_3)_6\text{Cl}_2$

30. The area is approximately 8.24 cm^2 by planimetry.

31. The area is approximately 21.2 cm^2 by planimetry.

$$32. \frac{(8.80 \text{ mcal sec}^{-1}) - (4.22 \text{ mcal sec}^{-1})}{(15.4 \text{ mg}) (0.167 \text{ }^\circ\text{C sec}^{-1})} = 1.78 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1} = C_p$$

The overall heat capacity is $2.73 + 1.78 = 4.51 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$

33. From the text: $\text{Area} = C' g \Delta M$

From the standard, C' is calculated as:

$$\frac{36.3 \text{ cm}^2}{(100 \text{ mg}) (4.63 \text{ kcal/mole})} = C'$$

The area for the ice should then be:

$$\frac{(36.3 \text{ cm}^2) (100 \text{ mg}) (1.43 \text{ kcal/mole})}{(100 \text{ mg}) (4.63 \text{ kcal/mole})} = 11.2 \text{ cm}^2$$

34. A sample of the mixture may be subjected to TG from room temperature to approximately 1100°C. The amount of copper can be determined from the decomposition below 470°C while decomposition after that will be related to the silver content. If the phase diagram for the alloy is known, the Ag/Cu ratio may be estimated from it.

$$\frac{(63.55 \text{ g/mol Cu}) (\Delta g_{\text{below } 470})}{(108.01 \text{ g/mol gas evolved})} = \text{g Cu present}$$

$$\frac{(107.87 \text{ g/mol Ag}) (\Delta g_{\text{above } 470})}{(62.00 \text{ g/mol gas evolved})} = \text{g Ag present}$$

35. The heat of neutralization is equal to the sum of the heat of ionization and the heat of the reaction of H^+ with OH^- .

$$\Delta H_{\text{reaction}} = \Delta H_{\text{ionization}} + \Delta H_{\text{H}_2\text{O}}$$

$$\Delta H_{\text{ionization}} = -10.2 \text{ kcal/mole} + 13.35 \text{ kcal/mole}$$

$$\Delta H_{\text{ionization}} = +3.2 \text{ kcal/mole}$$

36. a) The heat capacity of a system is simply the heat needed to raise the entire system by one degree Celsius. The heat needed is:

$$\frac{V_2 V_h t}{4.184 R_s} = \frac{(1.234)(1.876)(64.3)}{(4.184)(10.003)} = 3.56 \text{ calories}$$

$$\text{Heat Capacity} = \frac{3.56 \text{ cal}}{0.0235^\circ\text{C}} = 151 \text{ cal/}^\circ\text{C}$$

b) Since the same current flows through the standard and heater resistor, the calculated current (1.234 V/10.003 ohm) is 0.1234 amps. Using this and the voltage across

the heater, one obtains (1.876 V/0.1234 amp), a value of 15.20 ohms for the heater.

c) If the heater leads have an appreciable resistance, then the resistance of the heater itself must be less than 15.20 ohms. This means that less heat is being delivered to the calorimeter cell and the calculated heat capacity above is too high.

37. From the data given, the equivalence point should occur at 25 seconds. Using the equation in the text (Example 17.5):

$$K = \frac{[ML]}{[M][L]} = \frac{(0.0100)(8.68/10.0)}{[0.0100 - 0.0100(8.68/10.0)]^2} = 4.98 \times 10^3$$

Equilibrium constants may be calculated at other times also:

TIME	[M]	[L]	<u>K(x10⁻³)</u>	<u>ΔG(kcal)</u>	<u>ΔH(kcal)</u>	<u>ΔS(kcal mol⁻¹°C⁻¹)</u>
15	0.006	0.01	4.97	-5.05	-10.0	-16.6
20	0.008	0.01	4.96	-5.05	-10.0	-16.6
25	0.010	0.01	4.98	-5.05	-10.0	-16.6
30	0.012	0.01	4.92	-5.04	-10.0	-16.6
35	0.014	0.01	4.89	-5.04	-10.0	-16.6

The consistency of the above data is noteworthy, especially when compared to the results in the next problem.

38. With the data given, the endpoint occurs at 25 seconds, as in Problem 37.

$$K = \frac{ML}{[M][L]^2} = \frac{(0.0100)(8.68/10.0)}{[0.0100 - 0.0100(8.68/10.0)][0.0200 - 0.0200(8.68/10.0)]^2}$$

$$K = 9.43 \times 10^5$$

If the equilibrium constant is determined at different times as in Problem 37, the results are much different. The inconsistency indicates the wrong stoichiometry has been assumed. This is a rare occurrence, since the equivalence point would give another measure of the stoichiometry.

<u>TIME</u>	<u>[M]</u>	<u>[L]</u>	<u>K</u>	<u>ΔG(kcal)</u>	<u>ΔH(kcal)</u>	<u>ΔS(cal mol⁻¹°C⁻¹)</u>
15	0.006	0.02	2.62×10^7	-10.1	-5.0	+17.1
20	0.008	0.02	6.08×10^6	-9.26	-5.0	+14.3
25	0.010	0.02	9.43×10^5	-8.16	-5.0	+10.6
30	0.012	0.02	2.31×10^6	-8.69	-5.0	+12.4
35	0.014	0.02	2.81×10^7	-10.2	-5.0	+17.4

39. From the data given in the last two problems, it is obvious that Problem 37 has the correct stoichiometry.

CHAPTER 18

1. The first step is to work with the rate equation and, using the given data, extract values for the rate order on each species:

$d = c = 0$, since no products were present initially in any of the solutions.

$a = b = 1$, since by comparison of runs 1 and 2, doubling $[A]$ doubles the rate; and from runs 2 and 3, doubling $[B]$ doubles the rate.

Hence, under initial rate conditions, the following applies:

$-\frac{d[A]}{dt} = k[A][B]$, and the value of k can be calculated from the given data:

$$1.0 \times 10^{-3} \text{ M h}^{-1} = k (1.0 \times 10^{-3} \text{ M}) (1.0 \times 10^{-3} \text{ M})$$

$$k = 3.6 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$$

Now we can turn our attention to the catalytic determination of metal ion. First of all, in the catalytic determination, the $[B]_0$ or the $[A]_0$ is conveniently made sufficiently large that it can be considered to remain constant during the initial rate measurement.

Let's assume $[B]_0$ is about 100 times larger than $[A]_0$ (e.g., $1.0 \times 10^{-1} \text{ M}$), such as

for the uncatalyzed reaction: Initial Rate = $k'[A]$

and the rate coefficient for the uncatalyzed reaction is:

$$k' = k[B]_0 = 3.6 \times 10^5 \text{ sec}^{-1}$$

Recognizing that uncatalyzed rates take place simultaneously:

$$\text{Overall Initial Rate} = k'[A] + k'_c [A][X]_0$$

and we must calculate k'_c when $[X]_0 = 1.0 \times 10^{-8} \text{ M}$, considering a 10% error in the measurement step (C being the monitored species). Then:

$$-\frac{d[A]}{dt} = k' [A] + k'_c [A] [X]_0$$

and if the initial rate is based on a very small but finite change in signal and time, we can approximate by writing:

$$\frac{\Delta[A]}{\Delta t} = [A] (k' + k'_c [X]_0) \text{ or}$$

$$k' + k'_c [X]_0 = \frac{[A]}{[A]} \cdot \frac{1}{t}$$

$$[X]_0 = \frac{\Delta[A]}{[A] \Delta t k'_c} - \frac{k'}{k'_c}$$

Now, since a condition for reasonable success in catalytic determinations is $k' \ll k'_c$, we may simply write:

$$[X]_0 = \frac{[A]}{[A] \Delta t k'_c} \text{ or } k'_c = \frac{[A]}{[A] \Delta t [X]_0}$$

Values for Δt and $[X]_0$ are given, we must decide on $\Delta[A]$ and $[A]$ which are dictated by the tolerable error in their measurement and the molar absorptivity for C. Since we may equate the disappearance of A to the appearance of C,

$$k'_c = \frac{\Delta[C]}{[C]_t \Delta t [X]_0}$$

Also, since $[C]_0 = 0$, we may consider

$$[C]_t = \Delta[C] \text{ and}$$

$$k'_c = \frac{1}{60 \text{ sec} \times 1.0 \times 10^{-8} \text{ M}} = 1.7 \times 10^6 \text{ sec}^{-1} \text{ M}^{-1}$$

Regarding the molar level of C: From Sandell's book:

$$\% \text{ relative error} = \frac{30}{100 - \%T}$$

For 10% error, % T = 97.0 or A = 0.013, hence

$$[C] = \frac{A}{\epsilon b} = \frac{1.3 \times 10^{-2}}{(1.02 \times 10^3 \text{ cm}^2 \text{ mmole}^{-1})(1.0 \text{ cm})} = 1.3 \times 10^{-5} \text{ M}$$

2. Because $[I^-]_0 \gg [S_2O_8^{2-}]_0$, the rate can be expressed as a pseudo-first-order situation since $[I^-]_0$ can be considered to remain constant for all practical purposes:

$$\frac{d[S_2O_8^{2-}]}{dt} = -2.2 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1} \times 1.00 \times 10^{-2} \text{ M} [S_2O_8^{2-}]$$

$$\frac{d[S_2O_8^{2-}]}{dt} = -2.2 \times 10^{-5} \text{ sec}^{-1} [S_2O_8^{2-}]$$

Integrating: $\ln [S_2O_8^{2-}] = \ln [S_2O_8^{2-}]_0 - 2.2 \times 10^{-5} \text{ sec}^{-1} t$

$$t = \frac{\ln([S_2O_8^{2-}]_0/[S_2O_8^{2-}])}{2.2 \times 10^{-5}} \text{ sec}$$

For 10% reaction:

$$[S_2O_8^{2-}]_0/[S_2O_8^{2-}] = (5.00 \times 10^{-4} \text{ M}) / (4.50 \times 10^{-4} \text{ M}) = 1.11$$

$$t = \frac{\ln 1.11}{2.2 \times 10^{-5}} = 4.7 \times 10^3 \text{ sec}$$

$$t = (4.7 \times 10^3 \text{ sec}) / (3.6 \times 10^3 \text{ sec h}^{-1}) = 1.3 \text{ h}$$

3. At 50% reaction (fixed-time measurement) and at 75% reaction (method of tangents) the concentration of Ce(III) will be appreciable and the rate law does not simplify to a pseudo-first-order situation. The catalytic determination of iridium will be complicated. Under initial rate conditions (1-2% reaction) $[Ce(III)] \rightarrow 0$ and $k_3[Hg(I)] > k_{-2}[Ce(III)]$ and the rate law simplifies to

$$RATE = k_2 [Ir]_0$$

and the catalytic measurement can be easily handled. Moreover, the time required for determination will be conveniently short.

4. From Eqn. 18.22:

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] \approx 0$$

$$k_1[E][S] = k_{-1}[ES] + k_2[ES] = [ES](k_{-1} + k_2)$$

Moreover:

$$(1/K_M) = [ES] / ([E][S]) = k_1 / (k_{-1} + k_2)$$

Since $[E]_0 = [E] + [ES]$, $(IR)_{max} = k_2[E]_0$, and $(IR) = k_2[ES]$

we have:

$$[E] = [(IR)_{max}/k_2] - [(IR)/k_2] \quad \text{or}$$

$$K_M = \frac{[S] \{(IR)_{max} - (IR)\}}{k_2[ES]} ; \text{ since } (IR) = k_2[ES], \text{ we have}$$

$$K_M = [S] \{(IR)_{max} - (IR)/(IR)\} = \{ [S] (IR)_{max} / (IR) \} - [S]$$

$$K_M + [S] = [S] \{(IR)_{max} / (IR)\}; (IR) = [S] (IR)_{max} / (K_M + [S]) \quad [\text{Eqn. 18.23}]$$

and again, since $(IR)_{max} = k_2[E]_0$:

$$(IR) = (k_2[E]_0[S]_0) / (K_M + [S]_0), \text{ or } 1/(IR) = \frac{K_M}{k_2[E]_0[S]_0} + \frac{[S]_0}{k_2[E]_0[S]_0}$$

and finally:

$1/(IR) = K_M / k_2 [E]_0 [S]_0 + 1 / k_2 [E]_0$, plot of $1/(IR)$ vs. $1/[E]_0$ gives correct slope and intercept.

5. a) As indicated in Problem 4, k_2 gives an idea of the relative selectivity (specificity) of the enzyme toward a given substrate. The rate in substrate determination (in which the enzyme is not rate limiting) is:

$$(IR) = (k_2 [S]_0 [E]_0) / (K_M + [S]_0) = k_2' [S]_0$$

with $k_2' = k_2 [E]_0 / K_M$, which shows that the selectivity really depends on k_2 / K_M .

b) For substrate determination, $[E]_0$ is large and is not rate determining; hence, K_M gives an idea of the analytical region for substrate determination by initial rate measurements (See Figure 18.5), since $K_M = [S]$ if $(IR) = 1/2(IR)_{\max}$.

For enzyme activity measurement, $[S]_0$ must be large so that $K_M \ll [S]_0$ and $(IR) = k_2 [E]_0$; hence, inherently K_M does not affect the rate law for enzyme activity measurements, provided $K_M \ll [S]_0$

6. The initial rate at which the reaction starts toward equilibrium cannot be calculated simply by taking the difference between forward and reversed velocities as given by the respective Michaelis-Menten models derived for $[P] = 0$ or $[S] = 0$. To calculate the initial rate when neither $[P]$ nor $[S]$ is not zero, we must derive a different general rate equation, taking into account the reverse reactions:

$$(v)_{\text{net}} = k_2 [ES] - k_{-2} [E] [P] \quad (1)$$

with the following steady-state relationships:

$$(+ \frac{d [ES]}{dt}) = (- \frac{d [ES]}{dt}) \text{ or } \frac{d [ES]}{dt} = 0$$

Hence,

$$\frac{d [ES]}{dt} = k_1 [E] [S] + k_{-2} [E] [P]$$

$$- \frac{d [ES]}{dt} = k_2 [ES] + k_{-1} [ES]$$

$$k_1[E][S] + k_{-2}[E][P] = (k_2 + k_{-1})[ES]$$

$$[ES] = \frac{k_1[S] + k_{-2}[P]}{k_2 + k_{-1}} [E] \quad (2)$$

Dividing (1) by $[E]_0$, where $[E]_0 = [E] + [ES]$,

$$\frac{(v)_{\text{net}}}{[E]_0} = \frac{k_2[ES] - k_{-2}[E][P]}{[E]_0 [E] + [ES]}$$

Substituting $[ES]$ for its expression in (2):

$$\frac{(v)_{\text{net}}}{[E]_0} = \frac{k_2 \left(\frac{k_1[S] + k_{-2}[P]}{k_2 + k_{-1}} \right) [E] - k_2[E][P]}{[E] + \left(\frac{k_1[S] + k_{-2}[P]}{k_2 + k_{-1}} \right) [E]}$$

$$\frac{(v)_{\text{net}}}{[E]_0} = \frac{\frac{k_2 k_1[S]}{k_2 + k_{-1}} + \frac{k_2 k_{-2}[P]}{k_2 + k_{-1}} - \frac{k_{-2}(k_2 + k_{-1})[P]}{k_2 + k_{-1}}}{1 + \frac{k_1[S]}{k_2 + k_{-1}} + \frac{k_{-2}[P]}{k_2 + k_{-1}}}$$

$$(v)_{\text{net}} = \frac{[(k_2 k_1[S] [E]_0) / (k_2 + k_{-1})] - [(k_{-2} k_{-1}[P] [E]_0) / (k_2 + k_{-1})]}{1 + \frac{k_1[S]}{k_2 + k_{-1}} + \frac{k_{-2}[P]}{k_2 + k_{-1}}}$$

and finally

$$(v)_{\text{net}} = \frac{(v_{\text{max(forward)}} \frac{[S]}{K_{MS}}) - (v_{\text{max(reverse)}} \frac{[P]}{K_{MP}})}{1 + \frac{[S]}{K_{MS}} + \frac{[P]}{K_{MS}}}$$

in which $k_2[E]_0 = v_{\text{max}}(\text{forward})$

$k_{-1}[E]_0 = v_{\text{max}}(\text{reverse})$

and

$$K_{\text{MS}} = \frac{k_2 + k_{-1}}{k_1}; \quad K_{\text{MP}} = \frac{k_2 + k_{-1}}{k_2}$$

Note: The interested student is referred to "ENZYME KINETICS: Behavior and Analysis of Rapid Equilibrium and Steady-State Enzyme Systems" by Irwin H. Segel, Wiley-Interscience, New York, 1975, for more details of this and other situations in enzyme kinetics.

7. Using equivalents to Eqns. 18.39 and 18.40:

$$P_1 = G_{A,1}[A]_0 + G_{B,1}[B]_0 \quad (1)$$

$$P_2 = G_{A,2}[A]_0 + G_{B,2}[B]_0 \quad (2)$$

$$\text{From (1): } [B]_0 = (P_1 - G_{A,1}[A]_0) / G_{B,1}$$

Substituting in (2):

$$P_2 = G_{A,2}[A]_0 + (G_{B,2}P_1 - G_{A,1}G_{B,2}[A]_0) / G_{B,1}$$

$$[A]_0 = (P_2G_{B,1} - G_{B,2}P_1) - G_{A,2}G_{B,1} - G_{A,1}G_{B,2}$$

$$d[A]_0 = (G_{B,1}dP + G_{B,2}dP) - (G_{A,2}G_{B,1} - G_{A,1}G_{B,2})$$

and finally, the relative uncertainty in $[A]_0$ is given by:

$$d[A]_0 / [A]_0 = (dP[G_{B,1} + G_{B,2}]) / (P_2G_{B,1} - P_1G_{B,2})$$

which shows that the relative error in concentration depends on the values of the physical parameter being measured, P_1 and P_2 .

8. According to Steinhart's paper (Anal. Chem., 1979, 51, 1012), the emission of radiant

energy (fluorescence) is measured between 45 and 105 sec. after mixing reactants (tryptophan containing sample + formaldehyde in a pH 10.8 carbonate buffer). The difference between these two readings is directly proportional to the tryptophan concentration within certain limits that define the calibration curve. This is not a catalytic method nor a differential rate method; it is a single-component determination which plots a quantity proportional to the rate of light emission vs. the tryptophan concentration; as such, it is an approximation to the derivative approach.

9. Use logarithmic extrapolation approach. The intercept of the linear extrapolation of line 1 gives $[8\text{-quinolinol}]_0$. Since curve 3 corresponds to $4.0 \times 10^{-7} \text{ M}$ 8-quinolinol:

$$[8\text{-quinolinol}]_0 = \frac{(FI)_{i,1}}{(FI)_{i,3}} (4.0 \times 10^{-7} \text{ M}) = 5.7_1 \times 10^{-7} \text{ M}$$

where $(FI)_{i,1}$ = fluorescent intensity at intercept ($t = 0$) for line 1 = 30

and $(FI)_{i,3}$ = fluorescent intensity at intercept ($t = 0$) for line 3 = 21

The initial concentration of 5,7-dibromo-8-quinolinol can be calculated from the intercepts of curves 2 and 4:

$$[5,7\text{-Br}_2\text{-8-quinolinol}]_0 = \frac{(FI)_{i,2}}{(FI)_{i,4}} (1.0 \times 10^{-5} \text{ M}) = 1.1_3 \times 10^{-5} \text{ M}$$

$$(FI)_{i,2} = 62; (FI)_{i,4} = 55$$

10. (See the ref. given in the problem.)

a) The reaction is followed spectrophotometrically at 380 nm, where NiL^{2-} shows appreciable absorption (Zn^{2+} and ZnL^{2-} do not absorb appreciably).

b) Use a term called "apparent molar absorptivity":

$$\epsilon_{\text{NiL}_{\text{total}}} = [\epsilon_{\text{NiL}} + \epsilon_{\text{NiHL}} ([\text{H}^+]/K_{\text{NiHL}})] / [1 + ([\text{H}^+]/K_{\text{NiHL}})]$$

which allows one to calculate:

$$[\text{Ni}^{2+}] = [\text{ZnL}_{\text{total}}] = (A_i - A) / [b(\epsilon_{\text{NiL}_{\text{total}}} - \epsilon_{\text{Ni}})]$$

c) It is known that reaction 1 does not proceed far to the right even in presence of excess Zn^{2+} because:

$$K_{NiL} = 10^{18.6} \text{ and } K_{ZnL} = 10^{16.2}$$

and it is known that the zinc attack is fast.

d) The treatment requires measurement of initial rates since as the reaction proceeds the concentration of ZnL^{2-} increases, shifting the equilibrium of reaction 3 to the left. This reduces the amount of Cu^{2+} regenerated and thereby decreases the catalytic effect of Cu^{2+} .

e) When initial rates are studied, the observed first-order coefficient is:

$$K^* = k_{Cu}^{NiL} [Cu^{2+}]_0 + k_{Zn}^{NiL} [Zn^{2+}]_0$$

But $[Zn^{2+}] \gg$ any other species and can be considered a constant value during the runs, hence a plot of K^* vs. $[Cu^{2+}]_0$ should yield a straight line with:

$$\text{intercept} = k_{Zn}^{NiL} [Zn^{2+}]_0, \text{ and}$$

$$\text{slope} = k_{Cu}^{NiL}$$

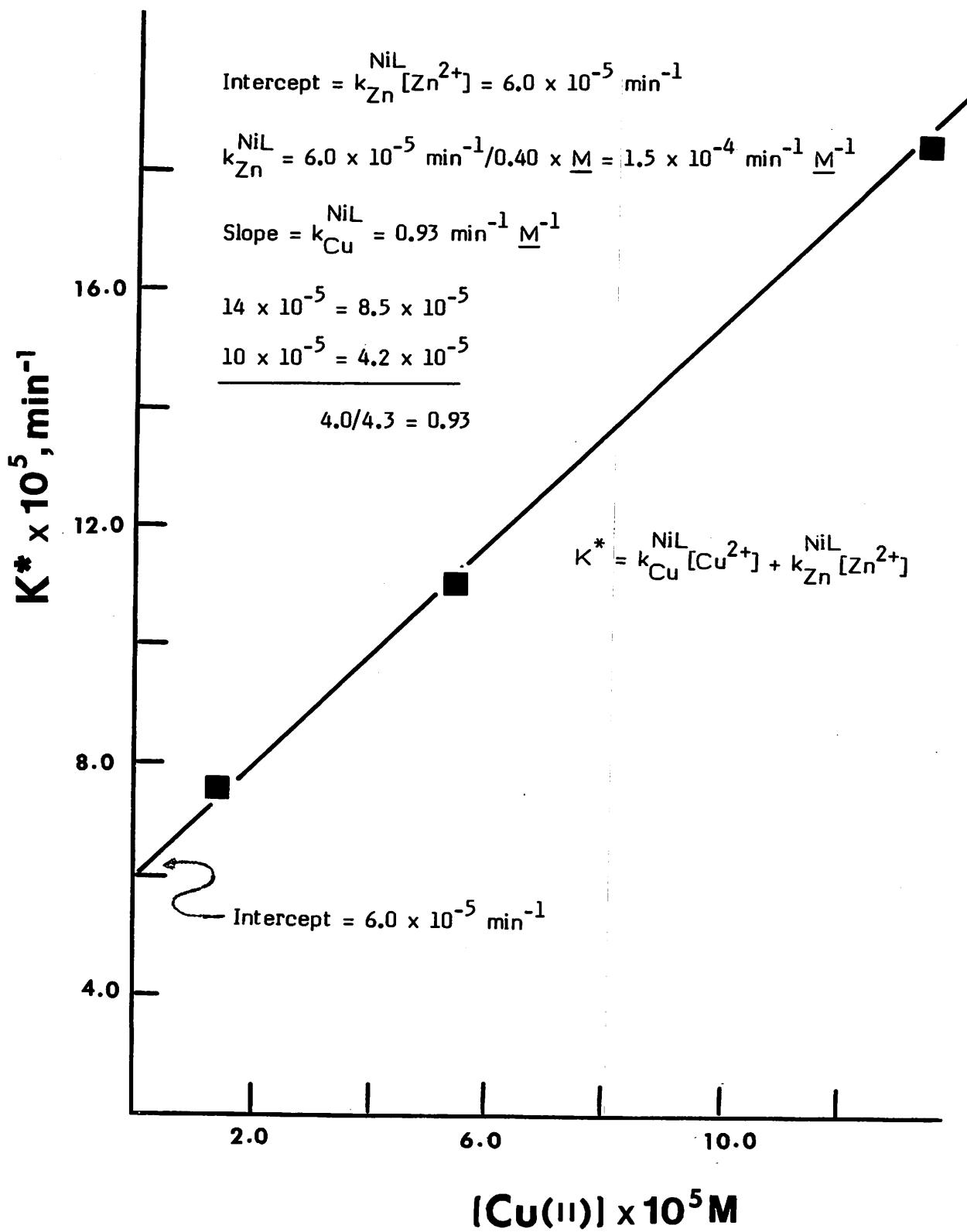
See adjacent graph which permits calculating the two rate constants. (Note: ϵ = molar absorptivities; K = equilibrium constants.)

11. With reference to the text in this chapter (Section 18.6, Instrumentation):

Special instrumental stability is required, such as light-source stability and low detector noise and drift. Provision for temperature control should be accessible in instrumentation to be used in reaction-rate methods. Also of consideration are the time constant of the instrument, the mode of transducer response, and the capability of peripherals for data-acquisition and handling, as well as control of automated operations.

12. Kinetic-based methods are commonly used in: a) catalytic determination of trace

10. Graph



amounts of metal ion species in solution (particularly transition metal ions), b) catalytic determination of substrate concentrations and enzyme activities (in enzyme catalyzed reactions), and c) simultaneous determination of closely related species by differential reaction rate methods.

13. Assume a mixture of \bar{A} , \bar{B} , and \bar{C} . Connors suggests a plot of $(A_\infty - A_t)e^{k_B t}$ vs. $e^{(k_B - k_C)t}$. After A has completely reacted, the plot becomes linear. (See Fig. 3 in the given reference.) with a slope of $[\bar{C}]_0$ and an extrapolated intercept equal to $[\bar{B}]_0 + [\bar{C}]_0$. Since $[\bar{C}]_0 + [\bar{B}]_0 + [\bar{A}]_0 = C_Z^\infty$, all three initial concentrations can be obtained.

C_Z^∞ : concentration of common product which must be known at the end of the reactions. Also, the individual rate coefficients must be known. The chemistry used was centered on the fact that the esters studied were p-nitrophenyl esters; the alkaline hydrolysis of these esters yields the common product p-nitrophenolate, which can be easily followed spectrophotometrically. The hydrolysis follows pseudo-first-order kinetics and facilitates the application of Connor's approach.

CHAPTER 19

1. Req. activity = 100 cpm at start of counting period

$$\text{Correct for 2 min decay: } 100 \text{ cpm} = C_0 \exp - \frac{0.693}{2.3 \text{ min}} (2 \text{ min})$$

$$C_0 = 183 \text{ cpm}$$

$$\text{Correct for efficiency: } \frac{183 \text{ cpm}}{0.1 \text{ cpm/dpm}} = 1830 \text{ dpm} = A_{\text{sat.}}$$

$$A_{\text{sat.}} = n f \sigma$$

$$\left[\frac{1830 \text{ dpm}}{60 \text{ sec/min}} \right] = \left[\frac{(g. \text{Al}) (\text{Iso. Abd. Frac.} = 1.0)}{(26.98 \text{ g/g-atom})} \times 6.023 \times 10^{23} \text{ at/g-atom} \right] \\ \times [2.0 \times 10^7 \text{ n cm}^{-2} \text{ sec}^{-1} \times 0.24 \times 10^{-24} \text{ cm}^2]$$

$$\text{Solve for g. Al} = 2.86 \times 10^{-4} \text{ g. Al/g. alloy} = 286 \text{ ppm}$$

2. a) The 5.62 MeV peak is due to the pair production interaction of the primary 6.13 MeV gamma ray with the crystal and the loss of one 0.511 positron annihilation photon from the crystal without interaction. This is the "1st escape peak."

b) The 5.11 MeV peak is due to loss of both 0.511 MeV annihilation photons resulting from a pair production event in the crystal. This is the "2nd escape peak."

c) The 0.511 MeV peak is due to pair production interaction of the 6.13 MeV primary gamma ray in the surroundings and shielding of the detector. The 0.511 MeV positron annihilation photons generated in the surrounding materials then intersect the crystal, yielding the observed 0.511 MeV peak.

3. Activity = $A = n f \sigma (1 - e^{-\lambda t})$

$$A_{\text{Mn}} = \frac{(\text{g. Mn})}{54.94} \times \text{AN} \times f \times (13.3 \times 10^{-24} \text{ cm}^2) (1 - e^{-0.693/2.57 \text{ h} (50 \text{ h})})$$

$$A_{\text{Fe}} = \left[\frac{(\text{g. Fe})}{55.85} \times \text{AN} \times f \times (0.33 \times 10^{-2} \text{ FIA}) (1.2 \times 10^{-24} \text{ cm}^2) \right] \\ \times \left[(1 - e^{-(0.693/45d \times 24 \text{ h/d}) (50 \text{ h})}) \right]$$

AN = Avogadro's number

FIA = Fractional Isotopic Abd.

f = Flux density ($n \text{ cm}^{-2} \text{ sec}^{-1}$)

$$\frac{A_{\text{Mn}}}{A_{\text{Fe}}} = 10^5 = \frac{(\text{g. Mn})}{(\text{g. Fe})} \left[\frac{55.85}{54.94} \right] \left[\frac{1}{0.33 \times 10^{-2}} \right] \left[\frac{13.3}{1.2} \right] \\ \times \left[\frac{(1 - e^{-13.48})}{(1 - e^{-0.0321})} \right]$$

Solve:

$$\therefore \frac{\text{g. Mn}}{\text{g. Fe}} = 0.926$$

4. Sp. Act. before electrol. for 5 ml of seawater

$$= 312,000 \text{ cpm} / (x \mu\text{g I}^-_{\text{seawater}} + 1 \mu\text{g I}^-_{\text{spike}})$$

% Chem. yield of plating pure spike soln

$$= (104,000 \text{ cpm plated} / 312,000 \text{ cpm added}) \times 100 = 33.3\%$$

\therefore same amount must be plated in cell with seawater

$$= 33.3\% \text{ of } 1 \mu\text{g I}^- = 0.333 \mu\text{g I}^-$$

$$\text{Sp. Act. of plate with seawater} = 20,800 \text{ cpm} / 0.333 \mu\text{g I}^-$$

$$\therefore 312,000 \text{ cpm} / (x \mu\text{g I}^-_{\text{seawater}} + 1) = 20,800 \text{ cpm} / 0.333 \mu\text{g I}^-, \text{ and}$$

$$x = 4.0 \mu\text{g I}^- / 5 \text{ ml seawater} = 0.8 \text{ ppm}$$

$$5. N_{12:30} = N_0 e^{-0.693/37.3 \text{ min}(30 \text{ min})} = 0.573 N_0$$

$$N_{1:30} = N_0 e^{-0.693/37.3 \text{ min}(90 \text{ min})} = 0.188 N_0$$

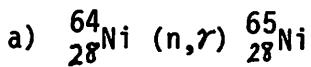
$$N_{12:30} - N_{1:30} = 100,000 \text{ cts.}$$

$$0.573 N_0 - 0.188 N_0 = 100,000$$

$$N_0 = 100,000/0.385 = 2.60 \times 10^5$$

6. Plot gives intersection with equivalence point at 25 ml of K_2CrO_4

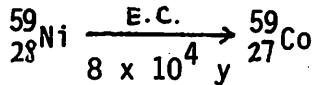
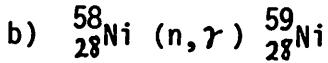
7. Possible reactions:



Irradiate in high flux nuclear reactor.

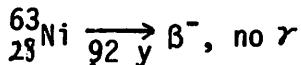
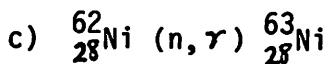
Advantages: Nuclear reactor thermal flux is high, readily available, cross section of ^{64}Ni (1.7 barn) is reasonably high. Good β emitter.

Disadvantages: Half-life is rather short and delay time before counting must be minimized. Little time for radiochemical separations. Natural abundance of target (^{64}Ni) is low limiting sensitivity.

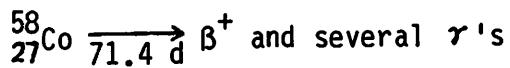
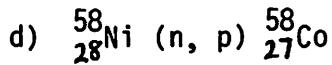


Advantages: High isotopic abundance of ^{58}Ni , high cross section of ^{58}Ni .

Disadvantages: Only decays by E. C., hence no energetic gamma rays emitted for counting. Would have to use x-ray counter. Long half-life of ^{59}Ni would yield low activity levels.



Arguments similar to b) above.



Advantages: Target ^{58}Ni has high isotopic abundance, reaction proceeds with reactor fast neutrons or 14 MeV neutrons from a neutron generator, half-life of product (^{58}Co) is long enough for radiochemical separations but short enough to yield reasonable activity, several gamma rays and annihilation radiation available for counting.

Disadvantages: (n,p) cross section would be lower than (n, γ) cross sections, fast neutron flux required.

Note: d) and a) are the best choices. d) is best if radiochemical separations are required.

8. Sp. Act. before plating

$$2 \text{ ml spike} \times 3 \text{ mg Co/ml spike} \times 1.50 \times 10^4 \text{ dpm/mg Co}$$

$$= 9.00 \times 10^4 \text{ dpm } ^{60}\text{Co added}$$

$$\text{Sp. Act. (before)} = \frac{9.00 \times 10^4 \text{ dpm}}{x \text{ mg Co steel} + 6 \text{ mg Co spike}}$$

$$\text{Sp. Act. (after)} = \frac{2500 \text{ dpm}}{(12.5 \text{ mg Co}_2\text{O}_3)(117.9 \text{ mg Co}/165.9 \text{ mg Co}_2\text{O}_3)}$$

$$\therefore \frac{9.00 \times 10^4}{x + 6} = \frac{2500 \text{ dpm}}{8.88 \text{ mg Co}}$$

$$x = 314 \text{ mg Co} = 0.314 \text{ g Co}$$

$$\frac{0.314 \text{ g Co}}{1.00 \text{ g steel}} \times 100 = 31.4\% \text{ Co}$$

$$9. \text{ Bkgd} - \frac{3600 \text{ cts}}{2 \text{ min}} = 1800 \text{ cpm}$$

$$\text{Samp} + \text{Bkgd} - \frac{6400 \text{ cts}}{2 \text{ min}} = 3200 \text{ cpm}$$

$$3200 \text{ cpm} - 1800 \text{ cpm} = 1400 \text{ cpm} \text{ net count rate}$$

$$\sigma_{\text{Bkgd}} = \frac{\sqrt{3600}}{2} = 30 \text{ cpm}$$

$$\sigma_{\text{gross}} = \frac{\sqrt{6400}}{2} = 40 \text{ cpm}$$

$$\sigma_{\text{net}} = \sqrt{(30)^2 + (40)^2} = 50$$

$$\therefore \text{Net rate} = 1400 \pm 50 \text{ cpm}$$

$$10. \text{ Sample A} + \text{Bkg} = 110 \text{ cpm}$$

$$\sigma = \frac{1100 \text{ cts}}{10 \text{ min}} = 3.3 \text{ cpm}$$

$$\text{Bkg} = 44 \text{ cpm}$$

$$\sigma = \frac{\sqrt{440}}{10} = 2.1 \text{ cpm}$$

$$\text{Net Count Sample A} = 110 - 44 = 66 \text{ cpm}$$

$$\sigma_{\text{net}} = \sqrt{(3.3)^2 + (2.1)^2} = 3.9$$

$$\text{Count Rate A} = 66 \pm 3.9 \text{ cpm}$$

$$\text{Sample B} + \text{Bkg} = 205 \text{ cpm}$$

$$\sigma = \frac{\sqrt{2050 \text{ cts}}}{10 \text{ min}} = 4.5 \text{ cpm}$$

$$\text{Net Count Sample B} = 205 - 44 = 161 \text{ cpm}$$

$$\sigma_{\text{net}} = \sqrt{(4.5)^2 + (2.1)^2} = \sqrt{20.25 + 4.41} = \sqrt{24.66} = 5.0 \text{ cpm}$$

Count Rate B = 161 = 5.0 cpm

$$\frac{\text{Count Rate A}}{\text{Count Rate B}} = \frac{66 \pm 3.9}{161 \pm 5.0} = 0.41 \pm \sigma$$

$$\sigma_{\text{ratio}} = 0.41 \sqrt{\left(\frac{3.9}{66}\right)^2 + \left(\frac{5.0}{161}\right)^2} = 0.0274$$

$$\therefore \text{Ratio} = 0.41 \pm 0.03 = A/B$$

11. $A = A_0 e^{-\lambda t}$

$$A/A_0 = 1/10$$

$$\ln 0.10 = -\lambda t = -0.693/t_{1/2} \times t$$

$$t = (\ln 0.10) (-5720 \text{y}/0.693) = 19,000 \text{ yrs old}$$

12. a) $3.70 \times 10^{10} \text{ atoms}$

b) Activity = (no. atoms present) (decay rate)

$$\text{decay rate} = \text{decay constant} = 3.70 \times 10^{10} \text{ dps}/2.67 \times 10^{21} \text{ atoms}$$
$$= 1.38 \times 10^{-11} \text{ sec}^{-1}$$

$$t_{1/2} = \frac{0.693}{1.38 \times 10^{-11} \text{ sec}^{-1}}$$

$$= 5.02 \times 10^{10} \text{ sec} \approx 1600 \text{ years}$$

13. a) 1 curie = $2.22 \times 10^{12} \text{ dpm}$

$$\therefore 2.22 \times 10^6 \text{ dpm} = 10^{-6} \text{ curies}$$

$$= 10^{-3} \text{ millicuries} = 1 \text{ microcurie}$$

b) $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{(3.82 \text{ days}) (8.64 \times 10^4 \text{ sec/day})}$

$$= 2.10 \times 10^{-6} \text{ sec}^{-1}$$

c) no. atoms = activity/decay constant

$$= 3.70 \times 10^4 \text{ dps}/2.10 \times 10^{-6} \text{ sec}^{-1} = 1.76 \times 10^{10} \text{ atoms}$$

d) no. grams = $1.76 \times 10^{10} \text{ atoms}/(6.02 \times 10^{23} \text{ atoms}/226 \text{ g})$

$$= 6.61 \times 10^{-12} \text{ g}$$

$$14. \text{ F.W.}_{\text{NaCl}} = 58.43$$

$$\text{g Na in } 0.02 \text{ g NaCl} = 22.98/58.43 (0.0200 \text{ g}) = 7.87 \times 10^{-3} \text{ g}$$

Atoms Na in 0.0200 g NaCl

$$= (7.87 \times 10^{-3} \text{ g}/22.98 \text{ g}) (6.02 \times 10^{23} \text{ atoms}) = 2.06 \times 10^{20} \text{ atoms}$$

$$1\% \text{ of } 2.06 \times 10^{20} = 2.06 \times 10^{18} \text{ atoms of } ^{24}\text{Na}$$

Activity = (atoms present) (decay constant)

$$= (2.06 \times 10^{18} \text{ atoms}) \frac{0.693}{(14.8 \text{ h}) (3600 \text{ sec/hr})}$$

$$= 2.68 \times 10^{13} \text{ dps}$$

$$\text{curies} = \frac{2.68 \times 10^{13} \text{ dps}}{3.70 \times 10^{10} \text{ dps/curie}} = 725 \text{ curies}$$

$$15. (2 \times 10^{-10} \text{ g}/74.99 \text{ g/mole}) (6.024 \times 10^{23} \text{ atoms/mole}) = 1.6 \times 10^{12} \text{ atoms}$$

$$A = Nc^4 [1 - \exp(-0.693t/t_{1/2})]$$

$$= (1.6 \times 10^{12} \text{ atoms}) (4.3 \times 10^{-24} \text{ cm}^2) (10^{13} \text{ neutrons/cm}^2\text{-sec})$$

$$(1 - \exp \frac{-0.693 \times 1 \text{ hr}}{26.5 \text{ hr}}) = 1.8 \text{ dps}$$

16. Maximum activity will occur when

$$(1 - e^{-\lambda t}) = 1.0$$

\therefore One-half maximum activity occurs when

$$(1 - e^{-\lambda t}) = 0.5$$

$$-\frac{0.693t}{t_{1/2}} = \ln 0.5$$

$$t = t_{1/2}$$

That is, one-half maximum activity occurs when the time of irradiation is equal to the half-life of the species being formed.

$$17. \text{ Average lifetime} = \frac{\sum(\text{all atoms}) \times (\text{individual atomic lifetime})}{\text{total number of atoms}}$$

$$= \frac{\int_{N_{t=0}}^{N_{t=\infty}} dN \times \int_{t=0}^{t=\infty} e^{-\lambda t} dt}{N_0}$$

$$= \frac{-(0 - N_0) \times [-1/\lambda(1/e^\infty - 1/e^0)]}{N_0}$$

$$\text{Ave. lifetime} = 1/\lambda$$

$$\therefore \text{Ave. lifetime} = \frac{t_{1/2}}{0.693} = 1.443 t_{1/2}$$

18. For biological labelling, high specific activities and small $t_{1/2}$ are desirable.

$$^{131}\text{I} \quad t_{1/2} = 8.041 \text{ d}$$

$$^{125}\text{I} \quad t_{1/2} = 59.7 \text{ d}$$

Specific Activity calculations: ($\mu\text{Ci I}/\mu\text{g HGH}$):

molecules HGH/ μg :

$$1 \mu\text{g} (1 \text{ g}/10^6 \mu\text{g}) (\text{mole}/21500 \text{ g}) (6.02 \times 10^{23} \text{ molec.}/\text{mole})$$

$$= 2.801 \times 10^{13} \text{ molec HGH}/\mu\text{g}$$

Since 1 atom I binds to each HGH, also have 2.081×10^{13} atoms I/ $\mu\text{g HGH}$

$$A = \lambda N$$

$$\text{for } ^{125}\text{I}: \quad A = [(0.693/59.7 \text{ d}) (1 \text{ d}/86400 \text{ s})] (2.081 \times 10^{13} \text{ atoms I})$$

$$= 3.763 \times 10^6 \text{ dps} (1 \mu\text{Ci}/3.7 \times 10^4 \text{ dps}) = 102 \mu\text{Ci}/\mu\text{g}$$

$$\text{for } ^{131}\text{I}: \quad A = [(0.693/8.041 \text{ d}) (1 \text{ d}/86400 \text{ s})] (2.081 \times 10^{13} \text{ atoms I})$$

$$= 755 \mu\text{Ci}/\mu\text{g}$$

$\therefore ^{131}\text{I}$ is the isotope of choice

$$19. \quad SA_1 = A_1/W_1^* \quad SA_2 = A_2/W_2$$

$$W_1 = (A_1/A_2)W_2 - W_1^*$$

$$W_1 = A_1 W_2 / A_2 - W_1^*$$

$$W_1 / W_1^* = A_1 W_2 / A_2 W_1^* - W_1^* / W_1$$

$$W_1 = W_1^* [(A_1 / W_1^*) (W_2 / A_2) - 1]$$

$$W_1 = W_1^* (S A_1 / S A_2 - 1)$$

CHAPTER 21

1. a) By Eqn. 21.3, $k' = n_x/n_m$, where n_s = moles of solute in the stationary phase and n_m = moles in the mobile phase. Since $R_f = n_m/(n_m + n_s)$, $R_f = 1/(1 + k')$.

b) $k' = 2.3$

c) Yes, R_f (estriol) = 0.27, R_f = 0.03 units apart

2. a) k' (o-nitroaniline) = 1; k' (m-nitroaniline) = 2; k' (p-nitroaniline) = 3.5

b) α (m-nitroaniline) = 2; α (p-nitroaniline) = 3.5

3. a) $R_f = a/b$, from Figure 21.4; R_f (3'-GMP) = 0.50, and R_f (2'-GMP) = 0.58

b) From Eqn. 21.10 and equation derived in Problem 21.1,

$$\alpha = \frac{k'(3'-GMP)}{k'(2'-GMP)} \text{ and } R_f = 1/(1 + k'), \text{ therefore}$$

$$\alpha = \frac{[1 - R_f(3'-GMP)][R_f(2'-GMP)]}{[1 - R_f(2'-GMP)][R_f(3'-GMP)]} = 1.4$$

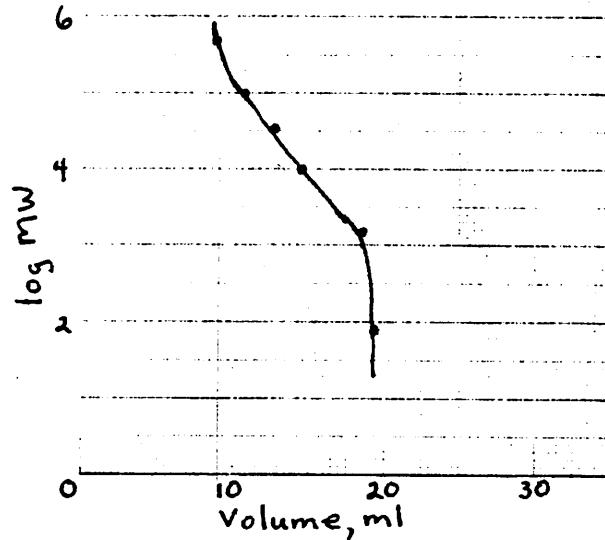
4. a) $\left(\frac{H_2}{H_1}\right) = \left(\frac{d_{p_2}}{d_{p_1}}\right)^{1.8}$ and Eqn. 21.7 $H = L/N$

$N = 64,000$ plates

b) By Eqn. 21.11, $R = 1/4 \sqrt{N} \left(\frac{\alpha - 1}{\alpha}\right) \left(\frac{k'}{1 + k'}\right)$

$R = 2.7$

5. a) See calibration curve:



b) $\text{Log MW} = 3.5; \text{ MW} = 3.2 \times 10^3$

c) Approx. 1000

6. a) $V_{\text{column}} = \pi r^2 L = 25 \text{ ml}; \text{Wt. of porous silica} = 13.8 \text{ g}$
 (from $V_{\text{column}} \times \text{packing density}$): $13.8 \text{ g} \times 2 \text{ mg/g} = 27.6 \text{ mg}$

b) $\text{Wt. of pellicular silica} = V_{\text{column}} \times \text{packing density} = 7.8 \text{ g}$

Capacity of column =

$$\frac{(\text{wt. of pellicular silica})(\text{surf. area of pellicular silica})}{(\text{surface area of porous silica})} 2 \text{ mg/g}$$

$$= 3.8 \text{ mg.}$$

c) Since L is proportional to V_s , $\frac{L_2}{L_1} = \frac{V_{s_2}}{V_{s_1}}$

$$\text{Therefore, } L_2 = \frac{L_1 V_{s_2}}{V_{s_1}} = 360 \text{ cm.}$$

d) $27.6 \text{ mg} \times 2/3 = 18.4 \text{ mg per injection;}$

$\therefore 200 \text{ mg}/18.4 \text{ mg/injection} = 11 \text{ injections}$

7. a) By (21.5) and (21.7),

$$k' = \frac{t_r - t_o}{t_o} \text{ and } H = L/N, v = L/t_o \text{ from above,}$$

$$\text{Solve for } t_r: \quad t_r = \frac{NH(1 + k')}{v}$$

b) $v_m = F(t_o)$ where F = flow rate, $t_o = 2$ min, and $v = L/t_o$,
 $v = 50$ cm/min

$$H = L/N \text{ and } N = L/H = 100 \text{ cm}/0.04 \text{ cm} = 2500 \text{ plates}$$

$$\text{Therefore, } t_r = \frac{(2500)(0.04 \text{ cm})(1 + 24)}{50 \text{ cm}/\text{min}} = 50 \text{ min}$$

8. Option (1)

$$\text{By Eqn. 21.13, } P \text{ is proportional to } L \text{ and } L_2 = \frac{N_2}{N_1} \cdot L_1 = 26.7$$

L_1 . Column length would be 26.7 m, which would be impractical, and pressure drop would be 267 atm, exceeding the system's limit.

Option (2)

By given equation and Eqn. 21.7, at constant d_p ,

$$\frac{H_1}{H_2} = \left(\frac{v_1}{v_2} \right)^{0.6} - \frac{N_2}{N_1}$$

Solving for v_2 . $v_2 = 0.04$ cm/sec, and since v is inversely proportional to time, t_r would be increased by a factor of $1/0.04$ or 250 times to 7500 min, too long to be practical.

Option (3)

$$\frac{N_2}{N_1} = \left(\frac{d_{p_1}}{d_{p_2}} \right)^{1.8}$$

Substituting and solving for d_{p_2} , we get $d_{p_2} = 8 \mu\text{m}$. By Eqn. 21.13,

$$(\frac{P_1}{P_2}) = (\frac{d_{p_2}}{d_{p_1}})^2, \text{ and } P_2 = 250 \text{ atm.}$$

Thus, this would be the desired option, since we can obtain the required number of plates, yet not exceed the pressure capabilities of the system. Also, the separation time will remain the same, since the velocity of the mobile phase remained the same.

9. a)	t_r (min)	t'_r (min)	k'	$\log k'$
void	1.57	---	---	---
benzene	5.56	3.99	2.54	0.41
naphthalene	10.65	9.08	5.78	0.76
anthracene	25.75	24.18	15.40	1.19

Plotting $\log k'$ vs. number and extrapolating gives $\log k'$ for naphthalene of almost 1.55. Therefore, $k' \approx 35.5$.

b) Increase flow rate, temperature; strengthen solvent; shorten column.

$$10. \Delta P = \frac{\phi \eta L v}{d_p^2} \quad v = \frac{\Delta P \cdot d_p^2}{\phi \eta \cdot L}$$

$$= \frac{(6000 \text{ psig})(10 \times 10^{-4} \text{ cm})^2}{(600 \text{ sec}^2/\text{cm})(2.0 \text{ cp})(30 \text{ cm})}$$

$$= \frac{(6000 \text{ psig})(70.308 \text{ g/cm}^2/\text{psig})(100 \times 10^{-8} \text{ cm}^2)}{(600 \text{ sec}^2/\text{cm})(2.0 \times 10^{-2} \text{ g/sec-cm})(30 \text{ cm})}$$

$$= 1.2 \times 10^{-3} \text{ cm/sec}$$

11. $V_m = 0.40 \pi r^2 L$ is the fraction of column occupied by mobile phase, where r is the internal radius of the column and L its length.

$$V_m = (0.40)(3.14)(0.20 \text{ cm})^2(25 \text{ cm}) = 1.26 \text{ cm}^3$$

$$V_r = V_m(1 + k') = 1.26 \text{ cm}^3(1 + 9.8) = 13.6 \text{ cm}^3$$

12. $A = \pi ab$

a) Standard: (10 μg 3'-GMP) $A = (3.14)(3.8)(5.9) = 70 \text{ mm}^2$

Unknown: (2' GMP) $A = (3.14)(3.0)(4.0) = 38 \text{ mm}^2$

$$\frac{70 \text{ mm}^2}{38 \text{ mm}^2} = \frac{10 \mu\text{g}}{x \mu\text{g}}$$

$$x = 5.4 \mu\text{g} 2' \text{ GMP}$$

b) $R_f = 42.5 \text{ mm}/76.5 \text{ mm} = 0.56$

13. a) Column 1: $R = 1/4 \sqrt{N} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k'}{1 + k'} \right)$

$$= 1/4 \sqrt{2 \times 10^4} \cdot \left(\frac{1.25 - 1}{1.25} \right) \left(\frac{3}{1 + 3} \right) = 5.3$$

Column 2: $R = 1/4 \sqrt{N} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k'}{1 + k'} \right)$

$$= 1/4 (2.56 \times 10^4)^{1/2} \left(\frac{1.05 - 1}{1.05} \right) \left(\frac{33.3}{34.3} \right) = 1.8$$

Therefore, column 1 shows better resolution.

b) $R \sim \sqrt{N}$ (column 1) = $R \sim \sqrt{2} = 1.4$ increase or 7.4

$$R \sim \frac{\alpha - 1}{\alpha}$$
 (column 2) = $R \sim \frac{2.10 - 1}{2.10} = \frac{1.10}{2.10} = 0.52$

(vs. 0.048 before)

$$\frac{0.52}{0.048} = 10.8$$

$$10.8 \times 1.8 = 19$$

Column 2 now gives better resolution.

14. From Eqn. 21.9, and measurement of the peaks

$$R = \frac{2(t_{R_B} - t_{R_A})}{t_{R_A} + t_{R_B}} = \frac{2(5.35 - 4.77 \text{ min})}{0.34 + 0.36 \text{ min}} = 1.7$$

15. a) Volume of columns = $\pi (d/2)^2 h$

Column A: $V = \pi (0.1 \text{ cm}/2)^2 (15 \text{ cm}) = 0.118 \text{ cm}^3 = 118 \mu\text{l}$

Columns B & C: $V = 520$ and $2,490 \mu\text{l}$, respectively

Column A total void volume: $V_m = t_0 F = 1.6 \text{ min} (50 \mu\text{l}/\text{min}) = 80 \mu\text{l}$

Column void volume = $80 \mu\text{l} - 20 \mu\text{l} = 60 \mu\text{l}$

% void inside column = $60 \mu\text{l} (100\%)/118 \mu\text{l} = 51\%$

b) Column B: $520 (51\%) = 265 \mu\text{l}$ in column + $20 \mu\text{l} = 285 \mu\text{l}$

Column C: total $V_m = 1290 \mu\text{l}$

c) $V_r = t_R F$

Column A: $V_R = 25.7 \text{ min} (50 \mu\text{l}/\text{min}) = 1285 \mu\text{l}$

Columns B & C: $V_R = 5660$ & $26800 \mu\text{l}$

Column A: $k' = (V_R - V_m)/V_m = (1285 - 80 \mu\text{l})/80 \mu\text{l} = 15.1$

Column B: $k' = [5660 - (285 + 20) \mu\text{l}] / (285 + 20) \mu\text{l} = 17.6$

Column C: $k' = 19.5$

16. For 1 ml of 55% acetonitrile/water

1.00 ml (0.55 ACN) (0.7828 g/ml) / (41.05 g/mole) = 0.0105 mole

1.00 ml (0.45 H₂O) (1.000 g/ml) / (18.02 g/mole) = 0.0250 mole

0.0355 mole (22.4 l/mole at STP) = 0.794 l gas

Column A: $50 \mu\text{l}/\text{min} (30 \text{ min}) (10^{-3} \text{ ml}/\mu\text{l}) (0.794 \text{ l}/\text{ml}) = 1.19$

1 gas = 1.2 l

Columns B and C have 4 and 20 times the flow rate,

respectively. They would produce 4.8 and 23.8 l of gas,
respectively.

CHAPTER 22

1. a) Changing carrier gas can affect the retention volume only if the fugacity of the solute is different in the new carrier gas. Nitrogen is a diatomic molecule and is more polarizable than helium and is more likely to have "non-ideal" interactions with polar molecules. All other things being equal, retention will decrease if nitrogen is used.

b) The effect on plate height will depend on the mechanism affected. The "B" term of the Van Deemter expression ($2Dg/u$) will decrease more rapidly if Dg is smaller, but if a mobile-phase resistance mass transfer term is important, then its effect will grow more rapidly in same situation. One might expect that the H_{min} would be smaller for nitrogen but that the slope of the RTMT part of the curve would be shallower for helium.

The use of a supercritical vapor at any reasonable pressure should reduce retention (more non-ideal interaction). The effect on plate height would be dependent on the effect of vapor density on solute diffusivity.

2. 1) Increasing the loading will increase load capacity but as the plate height is dependent on the square of the film thickness, this will increase plate height and reduce resolution somewhat. 2) Increasing the diameter but keeping the film thickness constant will improve mass transport while increasing sample capacity. Unfortunately, wide columns are harder to pack uniformly and flow near the walls is exaggerated. This reduces resolution.

3. a) $I = 100(\log 310 - \log 174)/(\log 373.4 - \log 174) + 100 \times 7$

$$I = 776$$

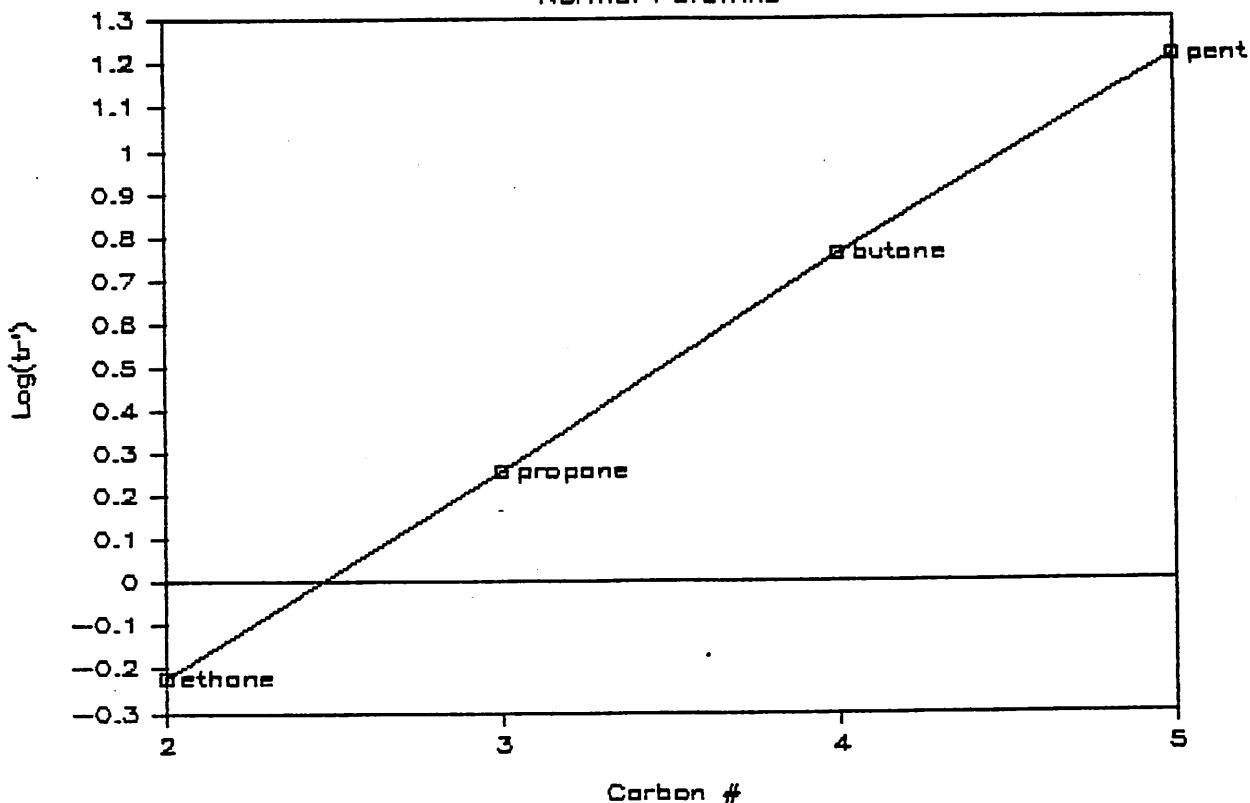
b) Only that n-butylacetate behaves in this system as if it were a hydrocarbon of 7.75 carbon-number. Structural information if better derived from the index increment ΔI ($I_{polar} - I_{nonpolar}$).

4. Methane is unretained.

All of the points do not fall on a single straight line. If we use chemical intuition and sort the compounds by class, then it can be seen that each class forms its own linear trend. The cis and trans forms of olefins are separate classes, as well. The accompanying figure shows the plot for normal paraffins.

Log(t_r') vs. C#

Normal Paraffins



5. Take first derivative and solve for H_{min} and u_{opt} .

6. Eddy effect - a molecule moves faster in the center of a stream than at the outside. Diffusion effect - the solute must spend some time in the mobile phase, and thus diffusion in the gas phase can take place. Resistance-to-mass-transfer - between the stationary and mobile phases. The three effects are represented in the A, B, and C factors in the Van Deemter equation (Eqn. 22.10).

7. See Problem 3 for setup. Toluene, 724; cyclohexane, 690.

8. For 80 psig,

a)
$$\frac{80 \text{ psig}}{(14.696 \text{ psig}/760 \text{ mm})} + 740 \text{ mm at outlet} = 4137 \text{ mm} + 740 \text{ mm}$$

$= 4877 \text{ mmg Hg} \equiv 4880 \text{ mm Hg}$

Similarly, for 20, 40, and 60 psig: 1770, 2810, and 3840 mm Hg.

b) $j = 1.5(R^2 - 1)/(R^3 - 1)$

R = inlet/outlet pressure

$$j = (1.5)(6.44^2 - 1)/(6.44^3 - 1)$$

$$R = 6.44$$

$$j = (1.5)(41.47/266) = 0.23$$

Similarly for 20, 40, and 60 psig: 0.56, 0.37, 0.28

9. 29.6, 50.0, 64.6 ml/min

10. a) $V_r' = 59.6, 226.8, 606.9 \text{ ml}$

b) $V_n = 16.7, 63.5, 170.0 \text{ ml}$

c) $V_g = 10.7, 40.9, 109.5 \text{ ml}$

d) 8.7, 9.2

e) Resolution = $2(t_{r_2}' - t_{r_1}')/(W_{b_2} + W_{b_1})$

$$R = 2(18.14 - 6.78)/(1.64 + 0.84)$$

$$R = 9.2$$

12. a) 4500 b) 6300 c) 9800 d) 39,000 e) 4400 f) 0.9, 1.3, 98, and 390 m

13. Careful measurement of the retention times for the six solute peaks from the methane peak on the far left produces the following ($t_0 = 3.10 \text{ min}$):

Peak	$t'_R \text{ (min)}$	$\log t'_R$
1	14.50	1.161
2	15.20	1.182
3	16.55	1.219
4	17.25	1.237
5	18.40	1.265
6	19.45	1.289

a) The problem now is to best fit the $\log t'_R$ values of the solutes to the carbon numbers: 1, 2, and 3 for the trifluoromethyl, pentafluoroethyl, and the heptofluoropropyl groups in $C_6H_5CH(CH_3)NHCOR$. Plotting $\log t'_R$ for peaks 1, 3,

and 5 and for 2, 4, and 6 produces two very straight parallel lines. Dividing the peaks into the two sets 1, 2, 3 and 4, 5, 6 and plotting versus carbon number produces somewhat poorer correlations, and the two lines are not as parallel. Other combinations do not produce linear plots. Therefore, peaks 1, 3, and 5 represent one set of enantiomers; and 2, 4, and 6 represent a second set. The assignments can also be rationalized by considering the relative magnitudes of the separation effects: Separation of enantiomeric pairs is difficult; the interactions of chiral centers are rather weak when compared to the magnitude of the separation effects expected for a change in molecular weight from addition of a CF_2 group (50 a.m.u.). Therefore, an enantiomeric pair ought to be expected to be separated by a smaller amount than would two members of a homologous series of the same handedness, even on a chiral phase.

The separations between peaks 1 and 2, 3 and 4, and 5 and 6 are about 0.7, 0.7, and 1.0 min. Whereas, the separation between alternate peaks is about 2.0 min. Therefore, peaks 1 and 2, 3 and 4, and 5 and 6 represent enantiomeric pairs; and peaks 1, 3, and 5 and peaks 2, 4, and 6 are the two sets of homologous series of different handedness.

b) From Eqn. 22.8, $\alpha = t'_{R_2} / t'_{R_1}$

For the enantiomeric pair in peaks 1 and 2,

$$\alpha = 15.20 \text{ min} / 14.50 \text{ min} = 1.048 = 1.05$$

Similarly $\alpha = 1.04$ for peaks 2 and 3, and 1.06 for peaks 3 and 4. The α value is roughly constant (1.049 ± 0.008) as would be expected.

c) Using Eqn. 22.8, and the facts that peaks 1, 3, and 5 are one series of the same handedness, and 2, 4, and 6 are of the other handedness:

$$\alpha_{1,3} = 16.55 \text{ min} / 14.50 \text{ min} = 1.14$$

Similarly, $\alpha_{3,5} = 1.11$; $\alpha_{2,4} = 1.13$; $\alpha_{4,6} = 1.13$

The separation between enantiomers is less than that between sequential numbers of the homologous series.

d) From Eqn. 21.9,

$$R = 2(t_{R_2} - t_{R_1}) / (t_{W_1} + t_{W_2})$$

For peaks 1 and 2, $R_{1,2} = 2(15.20 - 14.50) / (0.32 + 0.30) = 2.33 = 2.3$

For peaks 1 and 3, $R_{1,3} = 2(16.55 - 14.50) / (0.30 + 0.30) = 6.83 = 6.8$

e) From Eqn. 21.6,

$$N = 16(t_R/t_w)^2$$

$$N_1 = 16(17.6/0.3)^2 = 55,000 \quad \left. \right\}$$
$$N_2 = 59,500$$

$$N_{avg} = 57,300$$

From Eqn. 21.7,

$$H = L/N$$

$$H_1 = 40 \text{ m} (10^3 \text{ mm/m})/55,000 = 0.73 \text{ mm} \quad \left. \right\}$$
$$H_2 = 0.67 \text{ mm}$$

$$H_{avg} = 0.7 \text{ mm}$$

From Eqn. 21.5,

$$k' = t'_R/t_o$$

$$k'_1 = 14.50 \text{ min}/3.10 \text{ min} = 4.7$$

$$k'_2 = 4.9$$

f) From Eqn. 22.12,

$$R = (\sqrt{N}/4)(\alpha-1/\alpha)(k'/1+k')$$

$$= [(59,500)^{1/2}/4](1.048-1.000/1.048)(4.9/1+4.9) = 2.32 = 2.3$$

This compares very favorably with that in d).

CHAPTER 23

1. a) $V = IR$ $I = V/R = 5.00 \text{ V}/25.0 \text{ k}\Omega = 0.200 \text{ mA}$

b) $P = I^2R = V^2/R = (5.00 \text{ V})^2/25.0 \text{ k}\Omega = 1 \text{ mW}$

2. a) $R_T = R_1 + R_2 + R_3 = 0.100 \text{ k}\Omega + 0.500 \text{ k}\Omega + 1.00 \text{ k}\Omega = 1.60 \text{ k}\Omega$

b) $I = V/R_T = 8.00 \text{ V}/1.60 \text{ k}\Omega = 5.00 \text{ mA}$

c) $V_1 = IR_1 = (5.00 \text{ mA})(0.100 \text{ k}\Omega) = 0.500 \text{ V}$

$V_2 = 2.50 \text{ V}$

$V_3 = 5.00 \text{ V}$

3. a) Method 1: Resistors in parallel are inversely additive

$$1/R_p = 1/R_1 + 1/R_2 + 1/R_3$$

$$R_p = 1/(1/R_1 + 1/R_2 + 1/R_3) = 1/(1/100 \text{ ohm} + 1/500 \text{ ohm} + 1/1000 \text{ ohm}) \\ = 1/0.0130 \text{ ohm}^{-1} = 76.9 \text{ ohm}$$

Because $V = IR_p$,

$$I = V/R_p = 8.00 \text{ V}/76.9 \text{ ohm} = 0.104 \text{ A} = 104 \text{ mA}$$

Method 2: Do part b) first, then $I = I_1 + I_2 + I_3$

b) $I_1 = V/R_1 = 8.00 \text{ V}/100 \text{ ohm} = 80 \text{ mA}$

$$I_2 = V/R_2 = 8.00 \text{ V}/500 \text{ ohm} = 16 \text{ mA}$$

$$I_3 = V/R_3 = 8.00 \text{ V}/1000 \text{ ohm} = 8 \text{ mA}$$

$$I = 104 \text{ mA}$$

4. For the parallel combination of the 0.500 and 1.00 k Ω resistors, using Eqn. 23.11,

$$1/R_p = 1/500\Omega + 1/1000\Omega$$

$$R_p = 333\Omega$$

This is in series with the $0.100\text{ k}\Omega$ resistor. From Eqn. 23.6,

$$R_s = 333\Omega + 100\Omega = 433\Omega$$

The current through the whole circuit, from Eqn. 23.2

$$I = V/R = 8.00 \text{ V}/433\Omega = 18.5 \text{ mA}$$

and this will be the current through the $0.100\text{ k}\Omega$ resistor. The voltage drop across the resistor, Eqn. 23.1, is therefore

$$V = IR = 18.5 \text{ mA} (0.100 \text{ k}\Omega) = 1.85 \text{ V}$$

The power dissipation, Eqn. 23.5

$$P = I^2 R = (18.5 \text{ mA})^2 (0.100 \text{ k}\Omega) = 0.034 \text{ W}$$

The total current through the circuit, 18.5 mA, will be split between the parallel combination of the 0.500 and 1.00 k Ω resistors. The easiest way to calculate this is to remember that the voltage drop across the 0.100 k Ω resistor is 1.85 V. By Kirchhoff's voltage law, the voltage drop across the parallel combination, and across each resistor in the combination, must therefore be

$$8.00 \text{ V} - 1.85 \text{ V} = 6.15 \text{ V}$$

For the 0.500 k Ω resistor.

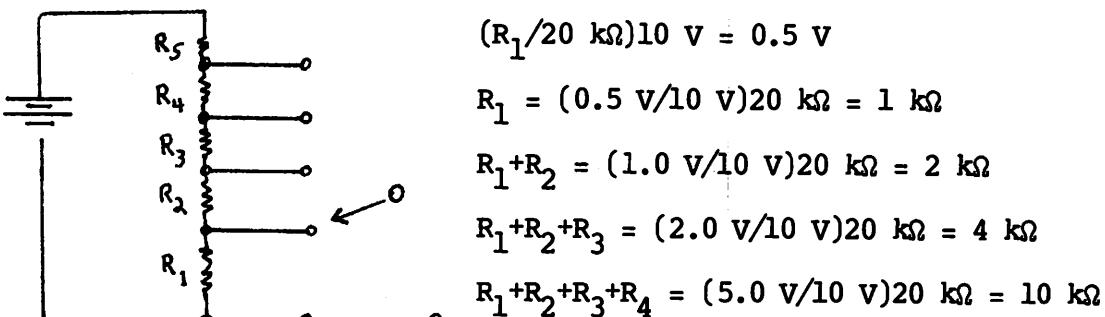
$$I = 6.15 \text{ V} / 0.500 \text{ k}\Omega = 12.3 \text{ mA}$$

$$P = (6.15 \text{ V})(12.3 \text{ mA}) = 0.076 \text{ W}$$

In a similar manner for the $1.00\text{ k}\Omega$ resistor.

$$I = 6.15 \text{ mA}; P = 0.038 \text{ W}$$

5. For the smallest resistor, R_1 , $[R_1/(R_1+R_2+R_3+R_4+R_5)] 10 \text{ V} = 0.5 \text{ V}$



$$R_5 = 20 \text{ k}\Omega - 10 \text{ k}\Omega = 10 \text{ k}\Omega$$

$$R_4 = 10 \text{ k}\Omega - 4 \text{ k}\Omega = 6 \text{ k}\Omega$$

$$R_3 = 4 \text{ k}\Omega - 2 \text{ k}\Omega = 2 \text{ k}\Omega$$

$$R_2 = 2 \text{ k}\Omega - 1 \text{ k}\Omega = 1 \text{ k}\Omega$$

6. From Eqn. 23.15,

$$v = V_p \sin \omega t$$

Because we want the absolute value of the average voltage, it is convenient to look at only one half cycle for a sinusoid. The average power would be the integral of $v(t)$ for a half cycle (π radians), divided by the time of the period

$$\begin{aligned} V_{\text{avg}} &= 1/\pi \int_0^{\pi} V_p \sin \omega t \, dt = V_p / \pi [-\cos \omega t]_0^{\pi} \\ &= V_p / \pi [-(-1) + (1)] = 2V_p / \pi = 0.637 V_p \end{aligned}$$

7. a) Take a series circuit consisting of a DC voltage source V and three capacitors - C_1 , C_2 , and C_3 . By Kirchhoff's voltage law, the voltage drop around the circuit must be zero

$$V - V_{C_1} - V_{C_2} - V_{C_3} = 0$$

But the voltage drop across a capacitor is $V_C = Q/C$.

Therefore,

$$V = Q_1/C_1 + Q_2/C_2 + Q_3/C_3$$

The charges, Q 's, on each capacitor must, however, be the same because the same amount of current must have flowed through all parts of the series circuit. Therefore,

$$V = Q(1/C_1 + 1/C_2 + 1/C_3) = Q(1/C_{\text{tot}}) = (1/C_s)$$

Therefore, for series capacitors

$$1/C_s = \sum 1/C_j = 1/C_1 + 1/C_2 + \dots$$

Capacitors in series are inversely additive.

b) Take the same three capacitors now in parallel. In this case, the voltage drop across each capacitor must be the same and equal to V . Each capacitor will require an amount of charge so that $Q_j = C_j V$ is true. The total charge passed is therefore

$$Q_{\text{tot}} = \sum Q_j = \sum C_j V = V \sum C_j = V C_{\text{tot}} = V C_p$$

Therefore, for a parallel network of capacitors

$$C_p = \sum C_j$$

Capacitors in parallel are directly additive.

8. a) $\omega = 2\pi f = 2\pi(60 \text{ sec}^{-1}) = 120\pi \text{ rad/sec} = 377 \text{ rad/sec}$

b) From Eqn. 23.14 $t = 1/f = 1/60 \text{ sec}^{-1} = 0.0167 \text{ sec}$

9. The capacitance of one electrode is $0.20 \text{ F/m}^2 (1.0 \text{ cm}^2) = 2.0 \times 10^{-5} \text{ F}$. The two 'capacitors' formed by the electrochemical double layers are in series, and are therefore inversely additive.

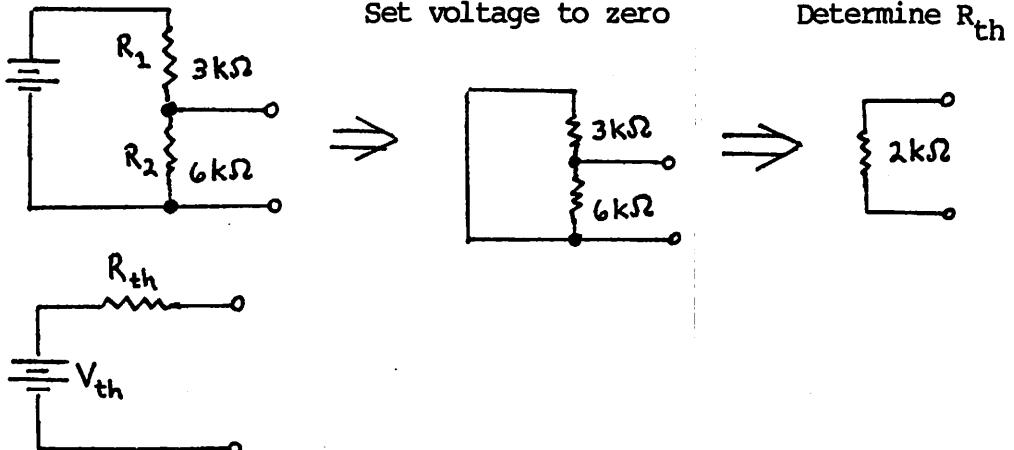
$$C_s = 1.0 \times 10^{-5} \text{ F}$$

Capacitive impedance, Eqn. 23.20, is

$$Z = X_C = 1/(2\pi f C) = 1/[2\pi(60 \text{ Hz})(1.0 \times 10^{-5} \text{ F})] = 265\Omega \text{ at } 60 \text{ Hz.}$$

At 1000 Hz, $Z = 16\Omega$

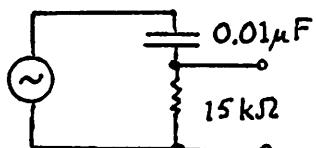
10.



$$R_{th} = R_1 R_2 / (R_1 + R_2) = (3.00 \text{ k}\Omega)(6.00 \text{ k}\Omega) / (3.00 \text{ k}\Omega + 6.00 \text{ k}\Omega) = 2.00 \text{ k}\Omega$$

$$V_{th} = R_2 / (R_1 + R_2) 6.00 \text{ V} = (6.00 \text{ k}\Omega / 9.00 \text{ k}\Omega) 6.00 \text{ V} = 4.00 \text{ V}$$

11. a)



b) $f_o = 1/2\pi RC = 1/[2\pi(0.01 \times 10^{-6})(1.5 \times 10^4)] = 1.06 \text{ kHz}$

c) $Z = \sqrt{R^2 + X_C^2} \quad X_C = 1/2\pi f C = 1/[2\pi(100 \text{ Hz})0.01 \times 10^{-6} \text{ F}] = 1.59 \times 10^5 \Omega$

$$= \sqrt{(1.5 \times 10^4)^2 + (1.6 \times 10^5)^2} = 1.6 \times 10^5 \Omega = 160 \text{ k}\Omega \text{ (at 100 Hz)}$$

Similarly, $Z = 22 \text{ k}\Omega \text{ (at 1 kHz)} = 15.0 \text{ k}\Omega \text{ (at 100 kHz)}$

d) The phase angle, $\Theta = \tan^{-1} (X_C/R)$

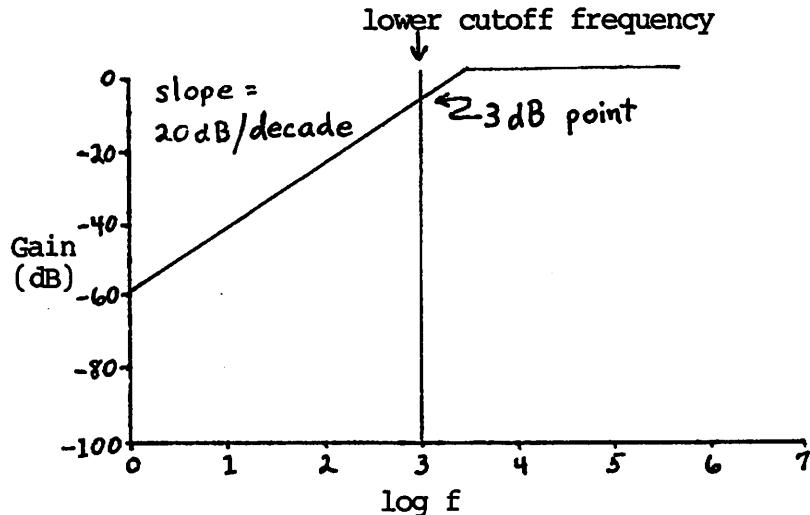
$$\text{At 100 Hz, } X_C = 1/2\pi fC = 1/2\pi(100 \text{ Hz})(0.01 \times 10^{-6} \text{ F}) \\ = 1.59 \times 10^5 \text{ ohm}$$

$$\text{and } R = 15 \times 10^3 \text{ ohm}$$

$$\Theta = \tan^{-1} (1.59 \times 10^5 / 15 \times 10^3) = \tan^{-1} (10.61) = 84.6^\circ \text{ or } 1.48 \text{ rad}$$

$$\text{At 100 kHz, } X_C = 159 \text{ ohm, } R = 15 \times 10^3 \text{ ohm and } \Theta = 0.011 \text{ rad or } 0.61^\circ$$

12.



13. a) For a series circuit, the impedances are directly additive.

$$Z_{\text{tot}} = R + 1/\omega C + \omega L = R + 1/2\pi fC + 2\pi fL \\ = 10 \text{ k}\Omega + 1/[2\pi(60 \text{ sec}^{-1})(10^{-6} \text{ F})] + 2\pi(60 \text{ sec}^{-1})(10^{-3} \text{ H}) \\ = 10 \text{ k}\Omega + 2.65 \text{ k}\Omega + 0.38\Omega = 12.65 \text{ k}\Omega$$

b) For a parallel circuit, the impedances are inversely additive.

$$1/Z_{\text{tot}} = 1/R + \omega C + 1/\omega L = 1/10 \text{ k}\Omega + 1/2.65 \text{ k}\Omega + 1/0.377\Omega = 2.65 \Omega^{-1}$$

14. b) From $i = I_i(e^{QeV/kT} - 1)$ $Z_{\text{tot}} = 0.377$

$$\ln i = \ln I_i + \ln(e^{QeV/kT} - 1)$$

$$\text{As } e^{QeV/kT} \gg 1, \ln(e^{QeV/kT} - 1) \approx QeV/kT.$$

The slope of the plot of $\ln i$ vs. V is Qe/kt , and the intercept = $\ln I_i = -17.03$. Thus, $I_i = 40$ nA.

c) Under reverse bias conditions $i \approx I_i = 40$ nA.

d) The small value for I_i is indicative of a silicon diode.

e) The very large current is unrealistic because joule heating would cause the device to self destruct.

15. a) $r = 1/(2\sqrt{3}fCR_L) = 1/[2\sqrt{3}(120 \text{ Hz})(2000\mu\text{F})(50\Omega)] = 0.0240 = 2.40\%$

b) $V_{\text{avg}} = 1.4 V_{\text{rms}} [1 - 1/(2fCR_L)]$

$$= 1.4(8.7 \text{ volts})[1 - [1/ 2(120 \text{ Hz})(2000 \mu\text{F})(50\Omega)]] = 11.7 \text{ volts}$$

16. $P = I^2R = IV \quad I = P/V = 0.25 \text{ W}/5.0 \text{ V} = 0.050 \text{ A} = 50 \text{ mA}$

17. Construct the load line from $I_C = V_C/R_L = 6 \text{ V}/500\Omega = 12 \text{ mA}$ and $V_C = 6 \text{ V}$.

From the characteristic curve of figure 23.19 (B) for $I_B = 40\mu\text{A}$, $I_C \sim 3.4 \text{ mA}$.

18. a) $V_o = -AV_s$ or $\Delta V_o = -A\Delta V_s \quad \Delta V_s = -\Delta V_o/A$

Neglecting the sign in this case, $\Delta V_o = + V_1 - (-V_e) = 2V_e = 24\text{V}$, so

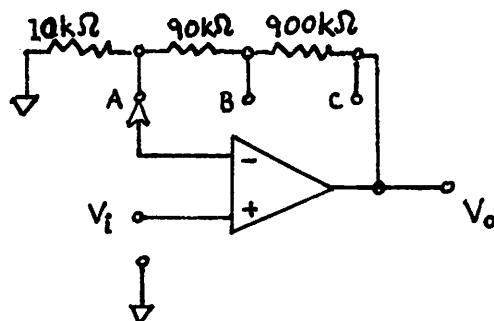
$$\Delta V_s = 24 \text{ V}/320 \text{ V/mV} = 0.075 \text{ mV}.$$

b) $t_{\text{slew}} = \Delta V_o/R_{\text{slew}} = 24 \text{ V}/12 \text{ V}/\mu\text{s} = 2.0 \mu\text{s}$

19. a) A follower with gain is appropriate with $1/b = (R_1 + R_2)/R_2 = 80$,

e.g., $R_1 = 70 \text{ k}\Omega$ and $R_2 = 10 \text{ k}\Omega$.

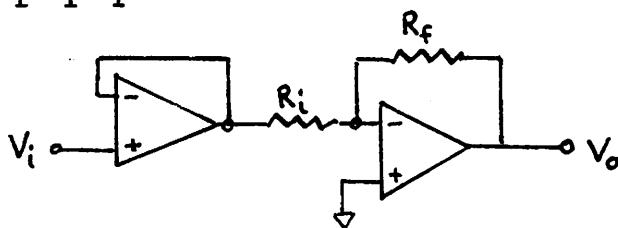
b) Use the decade voltage divider of Figure 23.8(a) as the feedback network as shown.



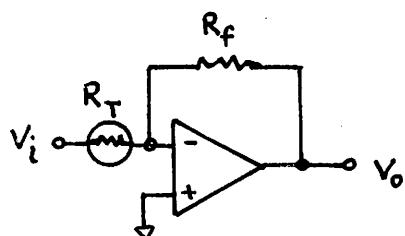
V_o/V_i	Switch Position
100	A
10	B
1	C

20. Use a follower to buffer the input of the inverter.

$$V_o = -(R_f/R_i)V_i$$



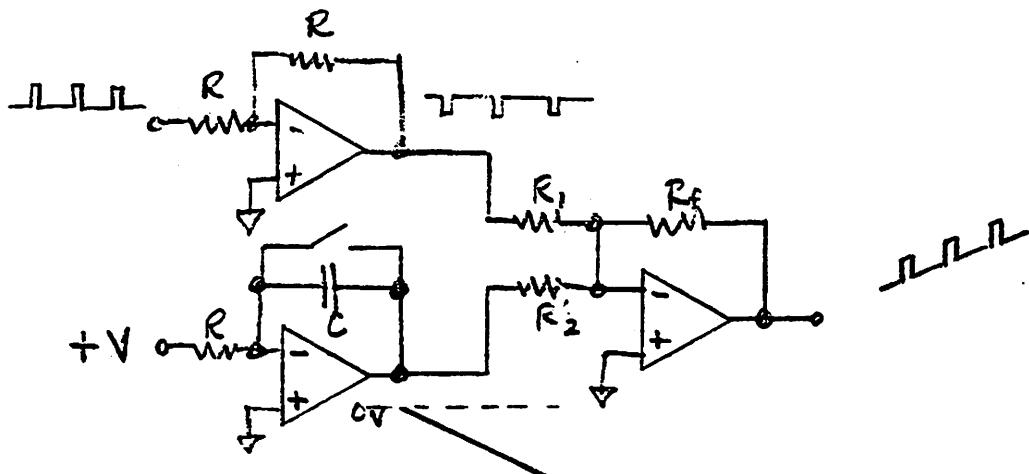
21.



$$V_o = -(R_f/R_T)V_i \text{ and } R_T = k/T$$

$$V_o = -(R_f/k/T)V_i = -(R_f V_i/k)T$$

22. a)

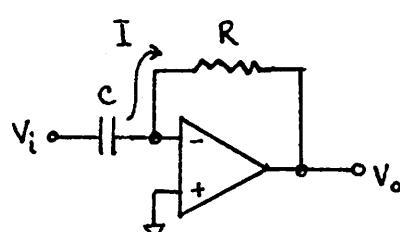


b) Change the size of R_1 relative to R_2 .

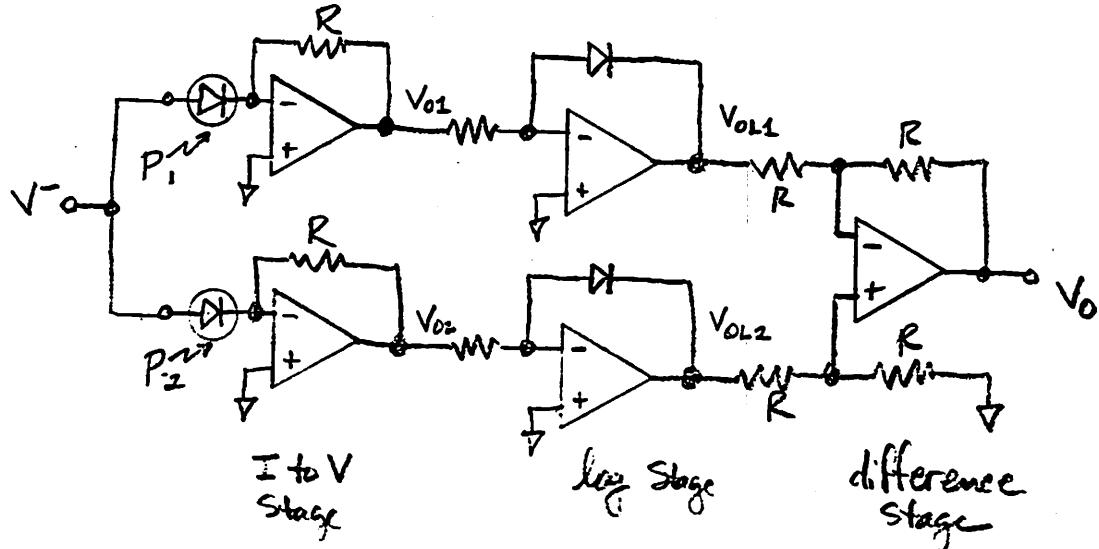
$$Q = CV_i$$

$$dQ/dt = C(dV_i/dt) \quad I = dQ/dt = -V_o/R$$

$$C(dV_i/dt) = -V_o/R \quad V_o = -RC(dV_i/dt)$$



24.



$$V_{01} = kP_1 \quad V_{0L1} = -\ln V_{01} + C \quad V_o = V_{0L2} - V_{0L1}$$

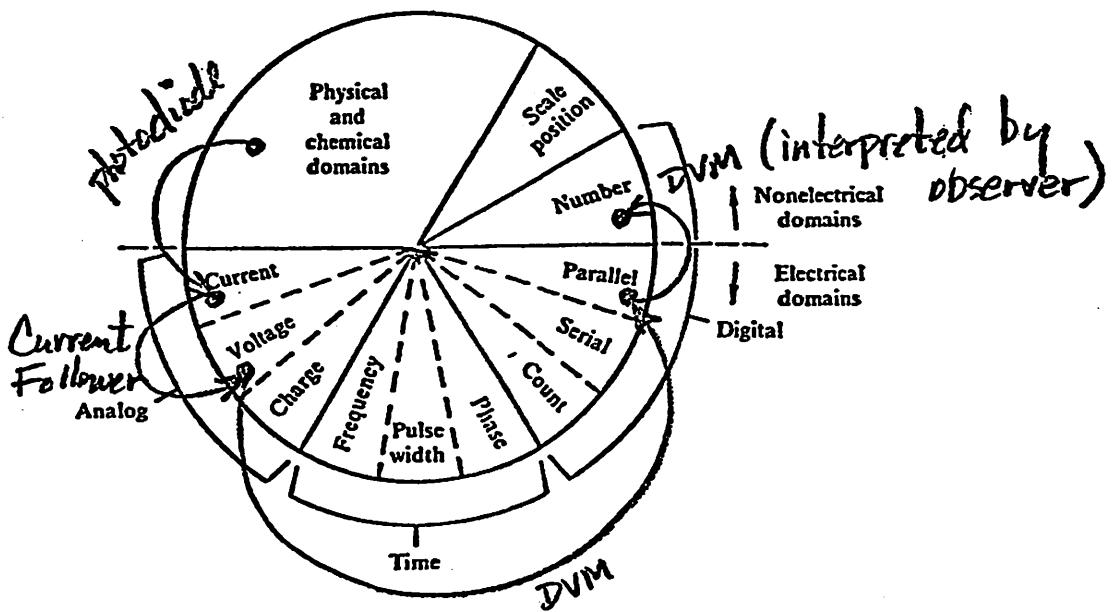
$$V_{02} = k'P_2 \quad V_{0L2} = -\ln V_{02} + C'$$

$$V_o = -\ln V_{02} - C' + \ln V_{01} + C = \ln(V_{01}/V_{02}) + (C - C')$$

$$= \ln(kP_1/k'P_2) + (C - C') = \ln(k/k') + \ln(P_1/P_2) + (C - C')$$

$$V_o = \ln(P_1/P_2) + C''$$

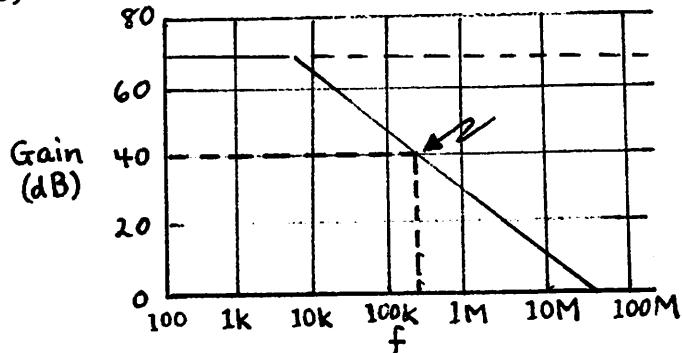
25.



26. a) $0.35/5\text{ns} = 70 \text{ MHz}$

b) $70 \text{ MHz} \times 1 = 70 \text{ mHz}$

c)



d) $\text{Gain} = (R_1 + R_2)/R_2 = 99 \text{ k}\Omega/1 \text{ k}\Omega = 100 = 40 \text{ dB}$

Graphically, the bandwidth = 700 kHz or from the gain - bandwidth product, $70 \text{ MHz}/100 = 700 \text{ kHz}$

27. An 8-bit device can represent the numbers from 0 to 255 with an uncertainty of 1. Therefore,

relative uncertainty = $1/256$ (100%) = 0.39%

For 10 bits,

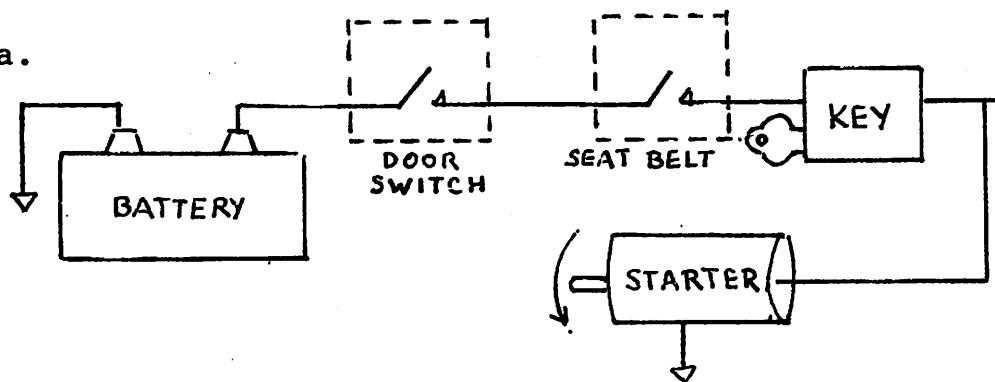
relative uncertainty = $1/1024$ (100%) = 0.10%

For 12 bits,

relative uncertainty = $1/4096$ (100%) = 0.024%

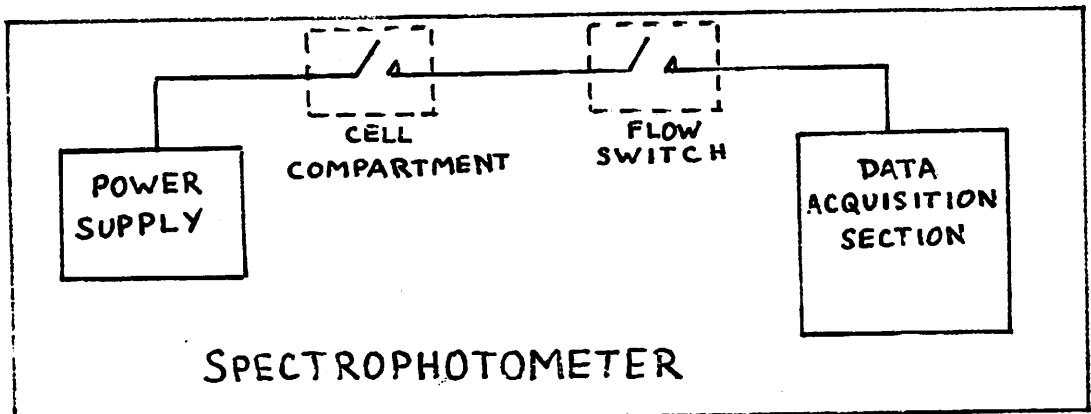
CHAPTER 24

1. a.



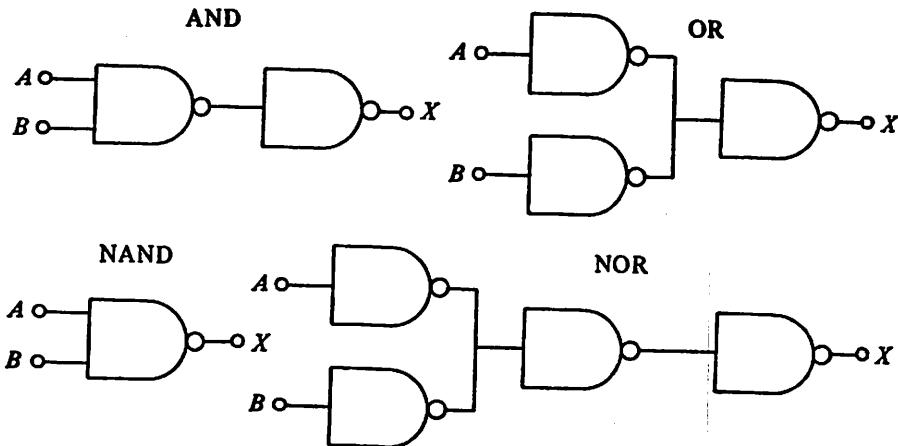
door closed \Rightarrow switch closed
 seat belt fastened \Rightarrow switch closed

b.

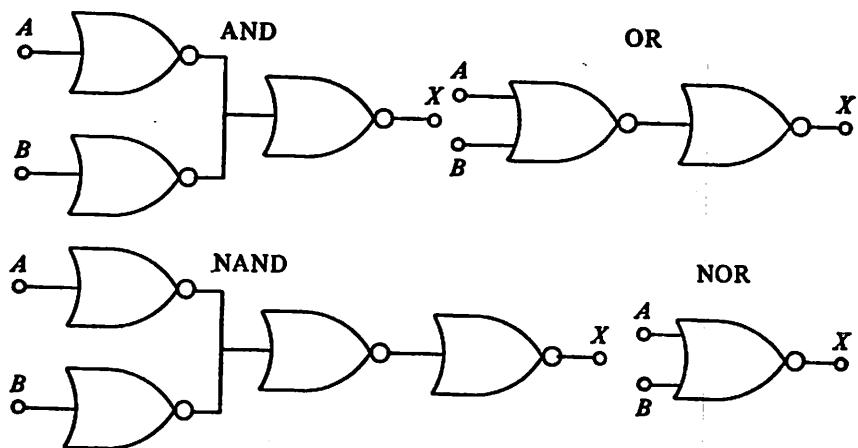


cell comp closed \Rightarrow switch closed
 water flowing \Rightarrow switch closed

2.



3.



4.

<u>A</u>	<u>B</u>	<u>\bar{A}</u>	<u>\bar{B}</u>	<u>$\bar{A} \cdot \bar{B}$</u>	<u>$A+B$</u>	<u>$\bar{A}+\bar{B}$</u>
0	0	1	1	1	0	1
1	0	0	1	0	1	0
0	1	1	0	0	1	0
1	1	0	0	0	1	0

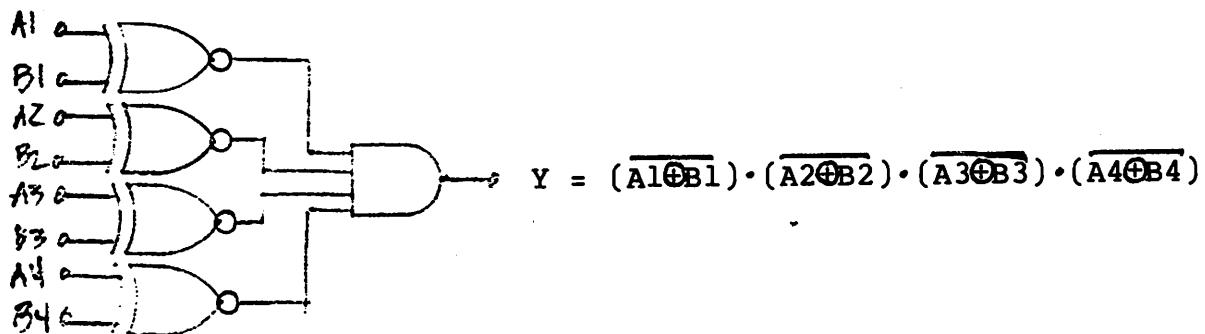
5.

<u>A</u>	<u>B</u>	<u>C</u>	<u>$X = A \cdot B + C$</u>
0	0	0	0
0	0	1	1
0	1	0	0
0	1	1	1
1	0	0	0
1	0	1	1
1	1	0	1
1	1	1	1

6. A B C $X = A \cdot \bar{B} \cdot \bar{C}$

0	0	0	0
0	0	1	0
0	1	0	0
0	1	1	0
1	0	0	1
1	0	1	0
1	1	0	0
1	1	1	0

7.



8. N Q_D Q_C Q_B Q_A

N	Q_D	Q_C	Q_B	Q_A
0	0	0	0	0
1	0	0	0	1
2	0	0	1	0
3	0	0	1	1
4	0	1	0	0
5	0	1	0	1
6	0	1	1	0
7	0	1	1	1
8	1	0	0	0
9	1	0	0	1
10	1	0	1	0
11	1	0	1	1
12	1	1	0	0
13	1	1	0	1
14	1	1	1	0
15	1	1	1	1

N	Q _D	Q _C	Q _B	Q _A
0	0	0	0	0
1	0	0	0	1
2	0	0	1	0
3	0	0	1	1
4	0	1	0	0
5	0	1	0	1
6	0	1	1	0
7	0	1	1	1
8	1	0	0	0
9	1	0	0	1

$$10. v_t^+ = (v_o^+ - v_{ref})(R_2/R_1+R_2) + v_{ref}$$

$$= (13V - 5V)(10\Omega/1.01k\Omega) + 5V = 5.079 \text{ V}$$

$$v_t^- = (v_o^- - v_{ref})(R_2/R_1+R_2) + v_{ref}$$

$$= (-13V - 5V)(10\Omega/1.01k\Omega) + 5V = 4.822$$

$$\Delta V = v_t^+ - v_t^- = 0.257 \text{ V}$$

$$11. v_t = v_o e^{-t/\tau}$$

$$v_t/v_o = e^{-3\tau/\tau} = e^{-3} = 0.050$$

$$12. a) 1/15 = 0.067$$

$$b) 1/15000 = 6.7 \times 10^{-5}$$

$$c) 1/150000 = 6.7 \times 10^{-6}$$

$$13. \text{ period} = 1/500 = 0.002 \text{ sec}$$

$$f_{\text{clock}} \geq 1/(0.002 \text{ sec} \times 0.2\%) = 250 \text{ kHz}$$

$$14. a) (6.74V/10V)100 \text{ kHz} = 67.4 \text{ kHz}$$

$$b) 67.4 \text{ kHz} \times 0.1 \text{ s} = 6740 \text{ counts, which is 4 digits}$$

$$c) \text{ Minimum voltage} = 1 \text{ count of 10,000 counts full scale, so}$$

$$\text{min. voltage} = (1/10000)10 \text{ V} = 0.001 \text{ V}$$

$$15. \text{ resolution} = 1/N$$

$$N = 1/\text{resolution} = 1/0.0002 = 5000$$

16. For the LSB, $-(10k\Omega/R_o)(-10.00 \text{ V}) = 0.01$

$$R_o = 10 \text{ M}\Omega$$

Likewise, $R_1 = 5 \text{ M}\Omega$, $R_2 = 2.5 \text{ M}\Omega$, and $R_3 = 1.25 \text{ M}\Omega$

17. Minimum conversion time requires 1 clock cycle or

$$1/100 \text{ MHz} = 0.01 \text{ } \mu\text{sec} = 10 \text{ nsec}$$

Maximum requires $2^{14} - 1$ clock cycles or

$$16384/100 \text{ mHz} = 163.84 \text{ } \mu\text{sec}$$

18. a) 32 states = $2^5 = 32$ bits

Requires a maximum of five trials, MSB = $2^5 - 1 = 16$

b) 16, 24, 20

c) 16, 8, 4, 6

d) 64 states = $2^6 = 64$ bits

Requires a maximum of six trials, MSB = $2^6 - 1 = 32$

e) 32, 48, 40

f) 32, 16, 24, 20

g) 32, 16, 8, 4, 6

19. Requires one clock cycle for each bit, so

$$t_{\text{tot}} = (10)(1/150 \text{ kHz}) = 66.7 \text{ } \mu\text{sec}$$

20. $\text{SNR} \propto \sqrt{N}$ $\text{SNR}_1/\text{SNR}_2 = \sqrt{N_1/N_2}$

$$N_1/N_2 = (\text{SNR}_1/\text{SNR}_2)^2 \quad N_1 = N_2(\text{SNR}_1/\text{SNR}_2)^2$$

a) $N_{50} = 100(50/10)^2 = 2500$

b) $N_{100} = 100(100/10)^2 = 10000$

c) $N_{1000} = 100(100/10)^2 = 10^6$

21. a) $s = \sqrt{\sum (x_i - \bar{x})^2 / N - 1} = 45.16$

$$\text{RSD} = 45.16/3212.8 = 0.01406 \quad \text{SNR} = 1/\text{RSD} = 71.1$$

$$b) (P-P)/5 = (3278 - 3159)/5 = 23.8$$

c) The result from b) is only a "ball park" estimate of the sample standard deviation.

22. The number of bits required is obtained from the power of two that is just greater than the number that represents the full scale reading, i.e., 1/resolution.

a) $1/0.002 = 500$ $2^9 = 512$, so 9 bits

b) $1/0.0002 = 5000$ $2^{13} = 8192$, so 13 bits

c) $1/0.00002 = 50000$ $2^{16} = 65536$, so 16 bits

CHAPTER 25

1. a) Heat capacity of water = 1 cal/g = 4.184 J/g

$$1 \text{ l H}_2\text{O} = 1000 \text{ g}$$

$$\text{so thermal cap.} = 4184 \text{ J/deg}$$

b) From Chem. Rubber Handbook:

$$\text{Thermal conductivity of building brick} = 5 \frac{\text{BTU}}{\text{hr ft}^2 (\text{°F/in})}$$

$$\text{or} \approx 25 \frac{\text{J}}{\text{cm}^2 (3600 \text{ sec}) (\text{°C/cm})}$$

so for a gradient of 1°C across a 5.0 cm thick wall 1 m², the flow of heat will be

$$(25 \text{ joule/cm}^2) (3600 \text{ sec}) (10^4) \approx 14 \text{ Joule/sec}$$

and the thermal resistance is 0.072 deg-sec/J

c) Air has an equivalent MW of 29, so at 25°C, and at 1 atm, 1 l of air has mass

$$1 \text{ l} \times \frac{29 \text{ g/mol}}{22.4 \text{ l/mol}} \times \frac{273}{298} = 1.19 \text{ g}$$

$$\text{Capacitance} = \frac{\text{Quantity}}{\text{Potential}} = 1.19 \text{ g/Pa}$$

<u>mv</u>	<u>pH</u>	<u>mv</u>	<u>pH</u>	<u>mv</u>	<u>pH</u>
+120	9	0	7	+180	10
+ 60	8	- 60	6	+120	9
0	7	-120	5	+ 60	8
- 60	6	-180	4	0	7
span 3 pH (180mv)	span 3 pH (180 mv)	span 2 pH (120 mv)			
range 6-9 pH	range 4-7 pH	range 8-1 pH			
(-60 - +120 mv)	(-180 - 0 mv)	(+60 - 180 mv)			
Elevated zero	Elevated zero	Suppressed zero			

3. a) Positive feedback augments an imbalance, therefore, control not possible.

b) Negative feedback reduces imbalance, therefore, regulation or control is made possible.

c) It would increase the heat when the temperature is above the set point or decrease the heat when the temperature is below the set point. The control loop would lock up at one extreme or the other.

4. Electric cookstove, electric oven, furnace, air conditioner, toaster, etc.

$$5. \text{ pH} = 1/2\text{pK}_w + 1/2\text{pK}_a + 1/2\log C = 7.0 + 2.38 + 0 = 9.4$$

Process gain is the incremental change in pH that occurs due to the incremental addition of reagent. It is inversely related to Buffer Index.

$$\text{a) Buffer Index} = \beta = 2.303 \left(\frac{K_w}{[H^+]} + [H^+] + \frac{CK_a [H^+]}{(K_a + [H^+])^2} \right)$$

At neutrality $\beta =$

$$2.303 \left(\frac{1 \times 10^{-14}}{4 \times 10^{-10}} + 4 \times 10^{-10} + \frac{(1)(1.75 \times 10^{-5})(4 \times 10^{-10})}{(1.75 \times 10^{-5})^2} \right)$$

$$= 1.2 \times 10^{-4}$$

and gain is nearly 10,000 at neutrality (8300).

b) At half titration point, $pH = pK_a = 4.76$

$$\beta = 2.303 \left(\frac{1 \times 10^{-14}}{1.75 \times 10^{-5}} + 1.75 \times 10^{-5} + \frac{(1)(1.75 \times 10^{-5})^2}{(3.5 \times 10^{-5})^2} \right)$$

$$= 2.303 (0.25) = 0.6$$

and gain is nearly 2 (1.7).

6. a) Sensitivity = $\frac{\Delta \text{output}}{\Delta \text{input}} = \frac{12 \text{ psi}}{50^\circ\text{C}} = 0.24 \text{ psi}/^\circ\text{C}$

b) Gain = 1, since full scale output charge is produced by full measurement interval.

c) %PB = 100 since the input must be changed over its entire range in order that the output change over its entire range.

d) At 50% proportional band, a 50% change in input would be required to change the output over its entire range. The gain would be 2 and the sensitivity would be $0.48 \text{ psi}/^\circ\text{C}$.

7. a) No effect

b) Doubling the gain

8. With the 100 ohm load, 4-20 mA becomes 0.4 to 2.0 volts. To this we must add gain and bias, so we can write

$$V_{\text{out}} = K V_{\text{in}} + V_B$$

where K is the gain and V_B is bias voltage. Since 0.4 volt input must give 10 volt output and 2.0 volt input must give 20 volt output, we can find K and V_B using simultaneous equations:

$$10 = 0.4 K + V_B$$
$$20 = 2.0 K + V_B$$

$$K = 6.25$$
$$V_B = 7.5$$

$$\text{Since } V_{in} = IR_L = 100I, V_{out} = 625 I + 7.5$$

9. The flow rate must increase to $1200 \text{ m}^3/\text{hr}$, and since the flow factor of the input valve is $20 \text{ m}^3/\text{hr}/\%$, this requires the controller output to be 60%.

From Eqn. 25.4, $e = (\text{output} - b) (\%PB/100) = (60-50) (10/100)$
 $= 1\%$

If the proportional band were increased to 20, the offset would be increased to 2%.

10. a) 50% of 10 volts or 5 volts to provide zero error controller output.

b) From 25.4: $(\text{output} - b) (20/100) = e$
$$\frac{40-50}{5} = -2\%$$

11. Reset time = $R_f C$

For $C = 100 \mu\text{F}$, $R = 100 \text{ k}\Omega$

For $C = 10 \mu\text{F}$, $R = 1 \text{ M}$

For PB = 25%, gain of 4 required, thus 1/4 or 0.25 the value of R_f to be fed back.

12. Full scale is 150°C ; $\pm 2\%$ of 150°C is $\pm 3^\circ\text{C}$

13. a) Multichannel, random access, batch, centrifugal or parallel fast, dedicated

b) Multichannel - measures many analytes in parallel or in sequence

Random access - measures, for each specimen, any analytes preselected from a menu; dedicated channels are not a characteristic

Batch - analyzes a batch of samples for a single analyte

Centrifugal - a variation of batch analyzer based on use of a centrifuge; particularly adaptable to kinetic measurements.

Dedicated - measures a specific analyte

14. Data display and printout, data processing, instrument self-monitoring, malfunction diagnostics, automatic control and sequencing

15. Temperature control, sensitivity at 340 nm, accurate absorbance scale, stable photometry at high absorbance values, high sensitivity and low noise

16. Na^+ , K^+ , Cl^- , CO_2 , Ca^{2+}

17. High sensitivity and specificity

18. Enzyme tagged (EMIT and ELISA), fluorescence tagged, nephelometry

